THE QUALITATIVE ANALYSIS OF MEDICINAL PREPARATIONS

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FOREWORD

This book is offered with the hope that it will be of as much assistance to other workers in the field of drug chemistry as it has been in manuscript form to my co-workers.

There is a mass of material in the text-books and literature dealing with the analysis of medicines, but it is an almost hopeless task for one who is starting out with an analysis to examine it all, and pick out what he needs for his particular problem. The gathering and sifting out of data, experimenting with new reactions, and the evolution of new and satisfactory tests have occupied the greater part of the author's time during the past five years, and it has been the endeavor to arrange the results of these investigations in such a way as to evolve a scheme of analysis which will tell the worker what to do and how to do it, and, when he gets his reactions, enable him to interpret the results.

Abundant use has been made of the material presented in the literature, and many of the tests collected and described in Allen's "Commercial Organic Analysis" have been adopted. Full acknowledgment is made here to the authors of this work, and also to Dr.

F. B. Power and his associates, whose researches have cleared up so many disputed points, and whose results have been of much assistance in compiling the accom- ıg data.

ı ıanks are due to those of my co-workers who have experimented with the scheme of analysis, and whose desire to have the material as a permanent record has led the author to finally offer it for publication.

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INTRODUCTION

DURING recent years the analysis of medicinal preparations has become very important, and there have been evolved many new methods for determining the active ingredients contained therein, as well as new reactions for the identification of different substances. In the latter case, the tests almost invariably apply to the substances in question when they are alone and in the pure condition, and take no account of the influence which might be exerted on the reaction if other things were present, a condition usually obtaining in attempting to identify the constituents of a complex medicine. Before one can, with any degree of certainty, proceed with the quantitative analysis, it is necessary to know the character of the components, and, up to the present, there has been no systematic scheme for obtaining this information. The Dragendorff and Stass–Otto methods of separation are satisfactory so far as they go, but they fall short of giving a complete analysis or separation of the manifold substances with which one has to deal when analyzing drug products.

From the analysis of several hundred mixtures, a scheme of separation has been gradually evolved by which the different substances are obtained at certain stages of the manipulation, and their identity established with a few readily applied tests. A knowledge of the use to which a particular preparation is to be employed is often a guide in arriving at conclusions as to its composition, and its price will often suggest what

might *not* be present; in fact, a drug analyst can, with advantage, be more than a chemist pure and simple—he should familiarize himself with the uses of the ordinary drugs, and have some idea of the current market conditions.

It is not the intention of this work to describe in detail the chemical and physical properties of the substances involved; as such data are available, it would be superfluous to repeat them here, and the laboratory should contain, for ready reference, the following works: U. S. Pharmacopœia; U. S. and National Dispensatories; "The Vegetable Alkaloids," Pictet & Biddle; "Plant Principles," Sohn; "Die Pflanzen Alkaloide," Brühl, Hjelt, and Aschan; "Die Glycoside," Van Rijn; "The Volatile Oils," Gildemeister and Hoffman; "Newer Remedies," Coblentz; Merck's Index; "Manual of Chemical Analysis," Newth. At times, the worker may meet with organic compounds which cannot be accounted for in this scheme, and for the possible identification of such he should refer to "The Identification of Organic Substances," Mulliken.

The work is divided in the following manner: The first portion describes the preliminary manipulation which separates the ingredients into large groups, then the scheme for separating these into smaller groups and individuals, and the tests for their identification; the second portion describes the methods to be employed in manipulating the various classes of medicinal products to make them available to separation in accordance with this scheme.

A diagrammatic arrangement, showing the essentials of the scheme at a glance, follows:

DIAGRAMMATIC SCHEME OF ANALYSIS

Original Substance. If a solid, extract with alcohol. If a liquid, evaporate and extract with alcohol.

Test original for arsenic.

- A. Alcohol-soluble portion. Treat with H_2O, and in a portion of this solution test for alcohol-soluble salts. Consult table.
  - a. Water-soluble portion. Add dilute H_2SO_4.
    - 1. Precipitated by acid, fatty acids, from soap, glycyrrhizinic acid.
    - 2. Solution. Shake out successively with: Petroleum ether; Ether; Chloroform.

      Add ammonia in excess, and shake with Petroleum ether; Ether; Chloroform; Alcohol-Chloroform.

      Residual solution may contain glycerin and other substances.
  - b. Water - insoluble portion. Resins, coloring matter. Treat with ether.
    - 1. Ether-soluble portion. Shake with 5% NaOH. Add acid, and shake with ether. Evaporate ether and test residue for resinous principles.
    - 2. Ether-insoluble portion. Make special tests. Consult table.
- B. Alcohol-insoluble portion. Treat with H_2O.
  - a. Water-soluuole portion. Evaporate.
    - Test for sugar and salts of acids altered by heat. Ignite and perform regular scheme of basic and acid analysis.
  - b. Water - insoluble portions. Treat with HCl.
    - 1. Soluble. Examine according to regular scheme of basic and acid analysis.
    - 2. Insoluble. Treat with HNO_3.
      - Soluble. Test for bases and acids.
      - Insoluble. Treat with Aqua Regia.

The Qualitative Analysis of MEDICINAL PREPARATIONS

FIRST PORTION

SCHEME OF ANALYSIS FOR THE SEPARATION AND DETECTION OF SUBSTANCES IN MEDICINAL PRODUCTS

Treat the residue, or ground substance, with alcohol, 95 per cent., stirring thoroughly, warming if necessary to get the material into solution, decanting the filtered liquid if any remains undissolved. Repeat several times, if necessary.

(*a*) Substances soluble in alcohol. Evaporate and treat the residue with water, filtering into a flask. Set aside one-third of the aqueous solution, then treat the solution with dilute acid.

(1) Substances soluble in water. Treat according to the scheme of separation described on page 12.

(2) Substances insoluble in water. Treat as described on page 68.

(*b*) Substances insoluble in alcohol. Treat with water and filter.

(3) Substances soluble in water. Treat as described on page 77.

(4) Substances insoluble in water. Treat as described on page 78.

By above process the substances mentioned below will have separated approximately into the respective groups:

(I) SUBSTANCES SOLUBLE IN WATER

Ammonium acetate
Ammonium carbonate
Calcium bromide
Calcium chloride
Gold chloride
Iron chloride
Mercuric chloride
Mercuric cyanide
Lithium bromide
Potassium bromide
Potassium thiosulphate
Potassium iodide
Potassium permanganate, decomposed by alcohol
Silver nitrate
Sodium acetate
Sodium arsenate
Sodium bisulphate
Sodium bromide
Sodium chlorate
Sodium thiosulphate
Sodium iodide
Sodium nitrate
Sodium nitrite, slightly sol. alcohol
Sodium sulphite, spar. sol. alcohol
Strontium bromide
Strontium iodide

Zinc chloride
Zinc bromide
Zinc iodide

Iron and quinine citrate
Iron and strychnine citrate
Lead acetate (partly sol. in alcohol)
Lithium benzoate
Lithium salicylate
Potassium citrate (spar. sol. in alcohol)
Soap
Sodium benzoate
Sodium salicylate
Sodium sulphocarbolate
Zinc valerate
Chloral hydrated
Guaiacol phosphate
Sublamine

Acetanilide (somewhat sol. in H_2O)
Acetozone
Adrenalin (sol. acids)
Alphozone
Acid salicylic
Acid benzoic
Acid citric
Acid tartaric
Antipyrine
Apiin
Aristochin (sol. acids)
Asaprol
Benzacetin (Acetamido-methyl-salicylic acid)

Benzoïn (Phenylbenzoyl-carbinol—bitter-almond-oil camphor)
Brometone, sol. H_2O
Bromural
Catechu
Chinaphenin (sol. acids)
Chrysarobin (sol. H_2O)
Convallamarin
Cotton-root bark resin
Coriamyrtin
Coronillin
Coryfin
Cyclamin
Epicarin (somewhat sol. H_2O)
Emodin (sol. alkaline sol.)
Eucalyptus gum—Red gum
Esculin
Ergotinin
Eugenoform (diff. sol. alcohol)
Eupatorin
Euphorin—acids
Euphthalmine—acids
Formanilide
Formicin
Gallanol
Gallicin
Gallobromal
Galloformin (diff. sol. in both H_2O and alcohol)
Gamboge (partly sol. in alcohol and H_2O)
Glycerin
Glycosal
Guaiamar

Hedonal
Ichthyol comps. (acids pptng. ichthyol)
Isopral
Kino
Lactucin
Lysidin
Manna (from alcohol deposits mannite on cooling)
Mesotan
Musk (partly)
Myrrh (partly)
Novaspirin
Novocain (sol. acids)
Orthoform
Oxaphor
Oxgall, purified
Periplocin
Phenacetin (slightly sol. in H_2O)
Phloridzin
Podophyllum resin (most of it is deposited by H_2O on cooling)
Resorcinol
Resorcylalgin
Salophen
Spirosal
Tannosal
Terpin hydrate
Thiocol (sl. sol. in alcohol)
Thiosinamine
Urethane
Valyl
Veronal

(2) SOLUBLE IN ALCOHOL AND INSOLUBLE IN WATER

(E denotes the substances which may subsequently be removed by ether)

Mercuric iodide (E)
Phosphorus (E)
Sulphur sublimed (E)

Difluordiphenyl (E)
Diiodoform
Ethyl diiodosalicylate (slightly sol. in water)
Ethyl iodide
Europhen
Iodoform (E)
Iodoformal
Iodonaphthol
Iron valerate (water decomposes it on boiling)
Nosophen (Tetraiodophenolphtalein—iodophenin) (E)
Orphol
Sanoform (E)
Terpene hydrochloride
Thymol iodide (E)
Tribromphenol (sol. ether)
Tribromsalol (sol. ether)
Trichlorophenol (sol. ether)

Acids (Glycyrrhizinic—precipitated by mineral acids)
Acids: Cerotic, Benzoic, Oleic, Palmitic, Salicylic, Stearic
Alantol (E)
Ammoniac (part sol. water; pt. E)

Amyl nitrite (almost insol. in water)
Anemonin (sol. in $CHCl_3$)
Apiol (E)
Arhovin (E)
Asafetida (milky emulsion with water)
Balsam Peru (E, partly)
Balsam Tolu (E, partly)
Benzoin
Benzyl cinnamate—Cinnamein
Benzosol—Guaiacol benzoate (E)
Betanaphthol salicylate (E)
Burgundy Pitch (E)
Bromoform (E)
Camphor monobromated (almost insol. in water) (E)
Cannabinon
Cardol
Cascarilla resin
Chlorophyll (E)
Chrysarobin (E)
Cantharidin
Cimicifuga resin (E partly)
Cinnamyl cinnamate (Styracin)
Cocain carbolate
Colophony (E)
Convallarin
Copaiba (E)
Creosote carbonate (E)
Cresalol (Cresol salicylate, E)
Damiana resin (E)
Eriodictyon resin (Yerba santa)
Eupyrin (sol. ether)
Filmaron (difficul. sol. alcoh., E)

Fluorescin
Fortoin (spar. sol. alcoh. & sol. alkalies, E)
Formopyrin (almost insol. alcoh.)
Formylphenetidin (sol. in hot water; E)
Galbanum (emulsifies with water; E)
Gallogen (insol. acids)
Grindelia robusta resin (E)
Gamboge (part. sol. alcohol; E por.)
Guaethol—Guaiacol ethyl
Guaiac (E partly)
Guaiacol carbonate—Duotal (sol. ether; E)
Guaiacol salicylate (E)
Hypnoacetin
Iatrol
Iothion (E)
Kamala (part. sol. alcohol; E)
Kamalin
Kosin (E)
Koussein
Losophen
Mastic (E)
Methylene diguaiacol—Geoform
Monotal
Naphthalene (E)
Naphthol (1–1000 in water; E)
Paraffin (E)
Phenacetin
Phenolphthalein (E)
Protosal (E)
Resin jalap (E partly)
Resin podophyllum
Resin scammony (E)

Salitannol
Sapogenin
Salit (E)
Salol (only very slight sol. H_2O; E)
Santonin (only very slight sol. H_2O; E)
Salacetol (only very slight sol. H_2O; E)
Scutellarin
Skatol (sol. hot water)
Storax (E partly)
Styracol—Guaiacol cinnamate
Sulphaminol
Styrene—Phenylelthylene (constit. of storax—sol. ether)
Tar (E)
Tannoform
Taraxacum resin
Tannopin
Trioxymethylene (sl. sol. H_2O)
Triphenin
Turpentine (E)
Validol—Menthol valerate (oil; E)
Valerydin—Sedatin
Wax (E)
Yerba Santa resin

(3) INSOLUBLE IN ALCOHOL BUT SOLUBLE IN WATER

Arsenous acid
Aluminum and potassium sulphate
Ammonium bicarbonate
Ammonium chloride (sl. sol. alcohol)
Ammonium phosphate

Antimony and potassium tartrate
Calcium thiosulphate
Iron pyrophosphate
Lithium carbonate
Potassium carbonate
Calcium hypophosphite
Potassium nitrate
Sodium bicarbonate
Sodium biborate
Sodium carbonate
Sodium chloride (sl. sol. alcohol)
Sodium hypophosphite
Sodium phosphate
Sodium pyrophosphate
Sodium sulphate
Zinc sulphate

Iron citrate
Iron and ammonium citrate
Iron and ammonium tartrate
Iron and potassium tartrate
Lithium citrate
Potassium bitartrate (sparingly in alcohol)
Potassium and sodium tartrate
Mercurol
Enesol (Mercury salicylarsenate)
Ferrostyptin (insol. cold alcohol)

Acacia
Citarin
Creatin
Erythrol (sol. alcohol)

Euquinin (sol. acids)
Gluconic acid
Hirudin
Papain
Pancreatin
Pepsin
Quininephytin (Quinine anhydro-oxymethylenediphosphate)
Saloquinine (sol. acids)
Sugar
Sulphanilic acid
Thiocol
Trioxymethylene

(4) INSOLUBLE IN ALCOHOL AND WATER

Bismuth subnitrate
Ammoniated mercury
Cerium oxalate
Mercurous iodide
Mercurous oxide
Mercuric oxide (very sl. sol. H_2O)
Mercurous chloride
Sulphur precipitated
Zinc carbonate
Zinc oxide
Zinc phosphide

Airol (Bismuth beta-oxyiodogallate)
Bismuth citrate
Bismuth subgallate
Crurin (Quinolin-bismuth sulphocyanate)

Cutal (Aluminum borotannate)
Dermol (Bismuth chrysophanate)
Ferratin
Iodalbin (almost insoluble)
Iodol
Sajodin (Calcium iodobehenate)
Triferrin (Iron paranucleinate)

Cantharidin (sol. hot alcohol; but deposits on cooling)
Gurjun balsam (part. sol. alcohol)
Lard
Starch
Spermaceti (sol. in hot alcohol; but deposits on cooling)
Tannalbin (sol. in alkalies)
Xeroform

Now proceed with the examination of No. 1, according to the following scheme of separation. It will be noted that the tables which follow, include some of the substances which were reported as being insoluble in water, but as the scheme is adapted to the procedures for examining the different classes of galenical products, the manipulation of which is detailed in the second section of the work, it is necessary to make provision for their occurrence.

(1) SUBSTANCES SOLUBLE IN WATER

Acid Solution

Note whether the solution is fluorescent.
Pichi, pink florescence with acids.
Quinin, blue florescence.

Sanguinarin gives a red solution without fluorescence. Shake out three times with petroleum ether, separate the solvent, wash it with water, and filter into a small beaker and evaporate over the steam-bath.

Alkaloids	*Bitter Principles*	*Acids*
Piperin 128°–129° Narcyl slightly	Absinthiin 120°–125° Capsacein Hop Bitter	Salicylic 136°–137° Benzoic 120°–121° Cinnamic 135° Picric (very slightly)

Acetanilide 113° Phenacetin (small amounts) 128°–129° Antipyrine (traces) 112°–113°	Cresol Thymol 50°–51° Menthol 243° Camphor 175° Terebene B–160°–180° Copaiba Cubebin 125° Santalol Cumarin 67° Vanillin 80°–81° Styrone (Cinnamic Alcohol) Odor of hyacinth. B-250°

Subcutin (somewhat) 195°–196°
Chloretone 80°–81°
Brometone
Epicarin (partly) 195°–199°
Chloral hydrated 58°
Neuronal 66°–67°
Sulphonal 125°–126°
Trional 76°
Veronal (slightly) 191°
Dormiol

Note the odor: *Camphor, menthol, copaiba, styrone, thymol, terebene, cubebol, santalol, coumarin*, and *vanillin* have characteristic odors. It should be noted, however, that most of these substances are but slightly soluble in water, and the first eight will appear in largest amount in the residue from the alcoholic extract, which is insoluble in water.

Remove a small quantity on the end of a glass rod or on the end of the finger, and touch the tongue.

Pungent sensation indicates *capsacein*, *piperin*.

Bitter taste indicates *hop bitter*, *absinthin*

Peppery sensation indicates *chloretone brometone*.

Numbness indicates *subcutin*.

If the residue is in considerable quantity, dissolve a portion in P.E.,* transfer to another dish, and evaporate. Cover the dish with a watch-glass, and place on a covered water-bath. Note any sublimate that collects on the watch-glass, indicating acetanilide, benzoic and salicylic acids. *Salicylic acid* sublimes more slowly than benzoic, and collects in quantity on the sides of the flask; benzoic collects in long stalactites having a brilliant lustre. *Cinnamic acid* does not sublime. Treat a portion of the sublimate with water, pour into an evaporating dish, and add a drop of ferric chloride solution; a purple color indicates presence of salicylic acid.

Treat a portion of sublimate or the material on the bottom of the dish with 5 c.c. chloroform and 2 c.c. of concentrated potassium hydroxide, heat carefully, note odor, the presence of *acetanilide* being indicated by the evolution of phenyl isocyanide.

Treat a portion of residue with dilute hydrochloric acid and water, placing a few drops on a water-glass, and adding Mayer's reagent; if a precipitate is obtained, *antipyrine* is indicated. To another portion of this solution add a few drops of potassium bromide-bromate reagent; if a blue color appears, *phenacetin* is indicated.

* This abbreviation denotes petroleum ether.

Treat a portion of the residue with 2 to 3 c.c. of cold 10 per cent. potassium permanganate solution, and warm slightly; if the odor of benzaldehyde develops, *cinnamic acid* is indicated.

Treat a portion of the residue with hot water, cool, filter, and treat with a few drops of ferric chloride; in the presence of *epicarin* an intense blue color develops. In making this test, the analyst must take into account whether or not salicylic acid had been previously indicated, or whether vanillin had been noted by the odor.

Treat a portion of residue with concentrated sulphuric acid; an orange-red color indicates *piperin*. This test cannot be depended upon unless the residue is white. Piperin should be crystallized out in P. E., and its melting-point determined—128° to 129°.

Treat a portion of the aqueous solution with ammoniacal silver nitrate, and warm. A reduction indicates *chloral* or *dormiol*.

Treat a portion of the residue with ammonium vanadate; a green color, changing to blue, quickly disappearing, indicates *subcutin*. Treat another portion with formaldehyde-sulphuric acid, which gives, with subcutin, a salmon color changing to brown.

Usually one is able to obtain sufficient of the crystallizable substances in the pure state to determine the melting-point, and when this figure is found, and corroborated by its characteristic reactions, the identity is established.

Benzoic acid may be separated from *salicylic* by dissolving both in dilute hydrochloric acid, adding excess of bromine water which precipitates the salicylic acid,

filtering, boiling off the excess of bromine, and shaking out the benzoic acid with ether or P. E.

Coumarin and *vanillin* may be separated by dissolving in ether, and shaking out with dilute ammonia, which will completely remove the vanillin. The ether is then evaporated, and the coumarin identified by its melting-point. The ammoniacal solution is then acidified, shaken out with P. E., separated, and the solvent evaporated, which leaves the vanillin in a form which can be readily identified.

Sulphonal, *trional*, and *neuronal* are best identified by their melting-points.

A solution of pyrogallol in pure 66 per cent. H_2SO_4 gives a blue color when gently warmed with *chloral*, a ruby color with *butylchloral*, and a more or less violet to blue color with mixtures. On adding a large amount of water, the blue color changes to yellowish, and the ruby to violet.

Shake out three times with ether, separate the solvent, wash it with water, filter into a small beaker, and evaporate over the steam-bath.

Acids*

Atropic 106°–107°
Camphoric 187°
Catechutannic
Cholalic
Creosotic, ortho 163°, meta 174°, para 151°
Diiodosalicylic 220°–230°
Formic

* The italics are used to call attention to the commoner substances.

Gallic 220°–240°
Gelsemic 163°–197° (?)
Lauric 43°
Lactic
Meconic
Monobrombenzoic, para 251°
Monoiodosalicylic 198°
Nitrobenzoic, ortho 147°, para 238°, meta 148°
Oenanthic 10°–11°
Oxybenzoic, meta 200°, para 210°
Protocatechuic 199°–200°
Succinic 182°
Tannic acid slightly
Tropic 117°–118°
Valeric
Veratric 182°

Glucosides

Anthemin
Asclepiadin
Collinsonin
Convallamarin slightly
Euonymin slightly
Helleborin
Hydrangin
Rutin
Scutellarin

* The italics are used to call attention to the commoner substances.

Alkaloids

Caffein, slightly, 236°
Colchicin
Narcotin, slightly, 171°
Theobromin 329°–330°
Narcyl, slightly

Anesthetics

Anesthesin, partly, 89°–91°
Orthoform, trace, 141°–143°
Propæsin 74°–76°
Subcutin 195°–196°

Plant Principles Not Glucosides or of Unknown Composition *

Arnica principle
Chiratin
Cnicin, slightly
Chrysarobin, partly
Colocynth bitter
Columbin, traces
Cotoin
Cotton-root resin
Elaterin, slightly
Emodin
Gentiopicrin, slightly

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* The italics are used to call attention to the commoner substances.

Ginger resins
Helenin
Hop resins
Lactucerin
Meconin 102°
Picrotoxin 192°
Podophyllotoxin
Santonin, partly 170°–171°

Acetanilide 113°
Acetozone 37° (?)
Alphozone
Antipyrine 112°–113°
Aspirin 135°
Bromacetanilide, para (Asepsin) 164°
Colchicein 149°–151°
Coryfin
Epicarin 195°–199°
Ethylacetanilide 50°
Gallanol (Gallic acid anilide) 205°
Gallicin (Gallic acid methyl ester) 202°
Heliotropin 37°
Phenacetin 134°–135°
Saccharin 220°
Saligenin (Diathesin) 86°
Salophen 187°–188°
Sapogenins
Sucrol (Dulcin) 173°–174°
Thymacetin 136°
Trioxymethylene 171°
Valyl (Valeric acid diethylamide)

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* The italics are used to call attention to the commoner substances.

Hypnotics *

Hydrated Choral
Bromal Hydrate 53°
Butyl Chloral Hydrate 78°
Dormiol
Chloral formamide 114°–115°
Chloralimide 155°
Chloralose 185°
Chloral urethane 103°
Euphorin (Phenyl urethane) 49°–50°
Neuronal 66°–67°
Veronal 191°
Propanol
Proponal 145°
Tetronal 85°
Trional 76°
Sulphonal 125°–126°
Methaform
Hedonal 76°
Hypnone 14°
Urethane 48°–50°
Ethylideneurethane 125°–126°
Bromural

Phenol and Phenol Derivatives *

Phenol 40°
Picric acid 122°–125°
Pyrogallol 132

* The italics are used to call attention to the commoner substances.

Methyl eugenol
Betanaphthol 122°
Creosote
Creosote phosphite (Phosphotal)
Creosote valerate (Eosote)
Fluorescein
Hydroquinon 169°
Phenolphthalein 250°
Phloroglucinol 200°–209°
Pyrocatechin 104
Resorcinol 109°–111°

Cantharidin 218°
Cholesterin 145°–148°
Coumarin 67°
Ichthyol
Lecithin
Vanillin 80°–81°

Certain substances which are present in the petroleum ether fraction will appear now, being incompletely removed by that solvent. Thus, if salicylic acid, antipyrine, acetanilide, neuronal, veronal, trional, sulphonal, and phenacetin were found in the residue left on evaporating petroleum ether, they will be found here.

Note the color. If yellow, draw off 2 c.c. into a test-tube, add 1 c.c. ammonia, and shake. If the ammonia turns pink or crimson, emodin or phenolphthalein is indicated. A pinkish-yellow color, gradually deepening with a more pronounced pink shade, will be observed if

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* The italics are used to call attention to the commoner substances.

aloes are present, this conclusion being further strengthened by a pronounced odor of aloes in the original material. A green fluorescence denotes the presence of gelsemic acid or esculin.

Evaporate the entire ether solution over the steam-bath, using a fan as the last portion evaporates, to prevent overheating, and note the quantity of the residue. Note whether there are needle-like crystals present, characteristic of caffein and theobromin. Note the odor, which will indicate the presence of ginger resins, phenol, guaiacol, ichthyol, vanillin, and coumarin.

Dissolve the last residue in ether, evaporate about ten drops, and test the residue cautiously by removing a small portion on the end of a rod or the finger. An intense sweet taste indicates saccharin. A numbness produced on rubbing the end of the tongue indicates propaesin, subcutin, and anesthesin. Note whether the residue has a bitter taste.

Remove five to ten drops onto a watch-glass, and evaporate. Treat residue with 2 c.c. dilute sulphuric acid, and warm; if the material does not completely dissolve, filter into another watch-glass. Add Mayer's reagent; a precipitate indicates antipyrine, colchicin, narcotin, the precipitate of colchicin being a deep yellow color.

Remove another five to ten drops, and evaporate in a porcelain evaporating-dish. Add one to two drops of concentrated sulphuric acid, and note the color.

Emodin, pink.

Elaterin, pink quickly changing to reddish-yellow.

Picrotoxin, yellow, orange, red on warming, and gradually a reddish-brown, while the solution becomes

fluorescent, observable on pouring the solution into a small test-tube.

Colocynth bitter, yellow-brown.

Cotoin crystals turn orange, while solution becomes bright yellow.

Meconin, pale yellow gradually becoming pale violet.

Convallamarin, brown, becoming deep purple on standing.

Santonin, yellow, with violet around isolated crystals.

Gentiopicrin, colorless, carmine on warming.

Gelsemic acid, yellow.

Narcotin, pale yellow, pink on edges, gradually red develops all through.

Many other substances give a brownish or a greenish-brown color, which is not characteristic.

Next remove five to ten drops, evaporate in a porcelain dish, and add one to two drops of Froehde's reagent.

Colocynth bitter gives a dirty red, red, cherry-red.

Elaterin, pink, yellowish-green, deep green.

Emodin, pink to red-pink.

Hydrastin, deep green.

Meconin, pale yellow, pale green.

Narcotin, deep green.

None of the other plant principles give characteristic colors.

Next remove five to ten drops, evaporate in a porcelain dish, and add one to two drops of ammonium vanadate reagent.

Meconic acid, purple, deep blue; gradually fades, very characteristic.

Colocynth bitter, red, blue in thin layers, pink, gradually deep crimson.

Elaterin, intense blue, soon fading to dirty yellow; undissolved crystals, orange, finally deep green, very characteristic.

Emodin, bright red, liquid soon turns brown.

Phenolphthalein, deep orange, pink on edges.

Meconin, crystals pale yellow at moment of solution; solution turns pale green, yellow, gradually pale red.

Subcutin, green to blue, disappearing quickly.

Santonin, no color.

Narcotin, brick red, pink in thin layers.

Propaesin, purple gradually fading to brown and gray.

Remove five to ten drops, evaporate in a porcelain dish, treat residue with two c.c. water, warm, then cool, and add two to five drops ferric-chloride test solution.

Green or greenish-black color indicates *tannins.*

Meconic acid, deep red.

Cotoin, violet-brown.

Aspirin, violet.

Phenol, blue.

Epicarin, blue.

Salicylic acid, violet.

Pyrogallol, orange-yellow.

Guaiacol, red, orange-red, slowly fading, and solution becoming turbid.

Hydroquinone, yellow-orange, green-black precipitate.

Phloroglucinol, blue-violet, violet fading rapidly.

Resorcinol, blue-violet.

Vanillin, blue.

Coumarin, no color.

Remove five to ten drops, evaporate in porcelain dish, add one to two drops concentrated nitric acid, and note reaction. Then evaporate and add alcoholic KOH.

Cotoin with HNO_3, deep blue, black, considerable action, brown-orange; very characteristic.

Santonin, no characteristic reaction with HNO_3, on evaporation and addition of alc. KOH, orange.

Asclepiadin with HNO_3, pink to purple.

Elaterin chars on adding HNO_3.

Subcutin on adding alc. KOH gives blood-red color and a fragrant odor.

Colchicin, blue.

Gelsemic acid, yellow, orange; add ammonia, which produces a blood-red color, very permanent.

Lead acetate gives ppts. with tannin, meconic acid.

If phenolic compounds are indicated (color reaction with $FeCl_3$) evaporate five c.c. of the ether solution in a test-tube, and fuse with NaOH and phthalic acid, cool residue, and add water.

Phenol gives phenolphthalein.

Guaiacol gives a solution violet-blue and violet.

Resorcinol gives fluorescin.

If sufficient material is present it should be purified by crystallizing out of water, alcohol, or other solvent, dried carefully, and melting-point determined.

If this scheme does not serve to identify the substances present, proceed according to Mulliken's scheme for the identification of organic bodies.

If saccharin is indicated by the sweet taste, and the residue gives a blue color with $FeCl_3$ indicating salicylic acid or other substances, treat a portion with dilute hydrochloric acid, warm, filter, cool, and add bromine

water, allow the ppt. to settle, then filter and wash. Boil filtrate until bromine is expelled, add a small piece of NaOH, evaporate the solution, fuse in an oil-bath to 250° C., cool, add water, and transfer to separator, add HCl and shake out with ether, evaporate ether, test residue with $FeCl_3$, when a violet color, due to formation of salicylic acid from saccharin, will be observed.

Dulcin may be differentiated from *saccharin* by dissolving in ether and shaking with alkali, which removes the saccharin; the ether is then washed, filtered, and evaporated, leaving the dulcin.

Test for *cantharidin* by dissolving a portion in alcohol and applying the solution to the arm, which will blister if this substance is present.

Santonin gives a red color with warm alcoholic KOH.

Anesthesin, *subcutin*, *propaesin*, anesthetic derivatives of amidobenzoic acid, all appear at this point.

Subcutin gives salmon gradually to brown with formaldehyde-sulphuric acid reagent, and green to blue color with ammonium vanadate.

Propaesin gives, with ammonium vanadate, a purple gradually fading to brown and gray.

Propaesin may be hydrolyzed by boiling with NaOH under a reflux; propyl alcohol is one of the products, and will be apparent because of its odor; from the alkaline solution mineral acids will precipitate the acid radicle.

Anesthesin does not give these reactions.

Aspirin differs from salicylic acid in giving no precipitate with bromine water.

Emodin dyes wool yellow; the color is stripped by ammonia, and gives a second dyeing. An alcoholic solution of emodin on evaporation with $FeCl_3$ leaves a

yellow residue; phenolphthalein under similar conditions leaves a pinkish residue, with odor of phenol, the color disappearing on cooling to moisture. Phenolphthalein goes on to wool, but there is no color imparted.

Veronal, *sulphonal*, *trional*, and *aspirin* give no immediate precipitates with iodine or picric acid, though with the latter reagent crystals will sometimes form on long standing.

Veronal sublimes on heating. If 1 to 2 c.c. of a saturated aqueous solution are treated with two drops nitric acid, and then with a few drops of Millon's reagent, a gelatinous white precipitate is obtained. When added to potassium hydroxide fused in a nickel crucible, and heated for two minutes, the cold mass, on dissolving in water, should give the Prussian-blue test with ferrous sulphate; on adding excess of acid, and shaking out with ether, an oily mass is extracted having the odor of rancid butter, soluble in water, the solution giving a wine-red color with ferric chloride.

Elaterin on fractionation yields a dextro- and levo-body or groups of bodies, the former being inert, the latter purgative.

Scutellarin, when treated with water and sulphuric acid, is dissolved with the formation of scutellarein, $C_{15}H_{10}O_6$, and glucuronic acid; on pouring the solution into considerable water the former is precipitated. Scutellarein dyes wool reddish-brown with chrome mordant, brownish-yellow with aluminum, lemon with tin, and olive with iron. The hydrobromide, hydrochloride, and sulphate are intensely colored. Glucuronic acid in dilute alcohol gives a green color when treated with alphanaphthol and concentrated sulphuric acid; with

more water the color changes through blue to violet, and even red, the green color being regenerated by adding concentrated sulphuric acid.

Scutellarin gives an orange-yellow barium salt.

Now shake out the acid solution three times with chloroform, when the following substances, if present, will go into solution.

Alkaloids *

Berberin traces
Caffein 236°
Colchicin
Geissospermin 160°
Hydrastin, partly 132°
Narcein, partly 145°
Narcyl base (Ethylnarcein)
Narcotin 171°
Oxyacanthin 210°
Papaverin 147°
Piperin 130°
Quebrachin 214°–216°
Theobromin 329°–330°

Glucosides and Plant Principles other than Alkaloids *

Adonidin
Anthemin
Columbin

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* The italics are sued to call attention to the commoner substances.

Cedrin
Condurangin
Daphnin
Digitoxin 240°
Elaterin
Gitalin 150°–155°
Emodin, somewhat
Helleborin
Menyanthin, glucoside from buckbean

Methylene Blue, very slightly
Betanaphthol benzoate 110°
Hippol (Methylenehippuric acid) 151°
Antipyrine 112°–113°
Phenacetin 134°–135°
Santoninic acid
Oxynaphtoic acid, alpha 186°, beta 156°
Physalin, from Physalis Alkekenga
Picrotoxin 192°
Piscidin
Quassin
Senegin, slightly
Polygalic acid, slightly
Strophanthin, slightly
Santonin 170°–171°
Strophanthidin

Evaporate the chloroform solution cautiously over the steam-bath, using fan, and note the appearance of the residue.

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* The italics are used to call attention to the commoner substances.

Methylene blue gives a blue color.
Berberin and *colchicin* give a yellow residue (the latter will have been indicated in the ether fraction).
Caffein and *theobromin* give needle-like crystals.
Taste residue, and note whether it is bitter, indicating *quassin* and *chrysarobin.*

Dissolve the residue in a small amount of chloroform, evaporate five to ten drops on a watch-glass, dissolve residue in one to two c.c. dilute sulphuric acid, and add Mayer's reagent; a precipitate indicates the presence of some alkaloid, but not caffein or theobromin. If no precipitate occurs, add one c.c. solution of iodine and potassium iodide; a precipitate indicates *caffein, theobromin,* and possibly other substances. If caffein was present in the original material, it would have been found to some extent in the ether fraction, unless it was present in very small amounts only. Antipyrine would have been previously indicated; piperin would have been found before, as well as chrysarobin, elaterin, emodin, picrotoxin, and santonin.

Evaporate five to ten drops of chloroform solution in a porcelain evaporating-dish, cool, add one to two drops concentrated sulphuric acid, and observe the color.
Narcein, deep brown at moment of solution, then yellow, gradually becoming green, and finally blue.
Narcotin, pale yellow, gradually pink on edges, and gradually a red color develops through the mixture.
Papaverin, pale violet, soon fading.

Quebrachin, blue color gradually develops, brought out more intensely by addition of lead peroxide or $K_2Cr_2O_7$ (in the latter case the mixture soon turns brown).

Geissospermin, blue.

Columbin, orange changing to deep red.

Hydrastin gives a faint yellow, deep purple on heating. If a trace of HNO_3 is present, a yellow color is produced, and with a larger proportion the color is orange-red.

Chrysarobin, deep red.

Digitalis glucoside, red, more intense on warming; expose to fumes of bromine and a violet color appears.

Elaterin, pink quickly changing to reddish-yellow.

Emodin, pink.

Picrotoxin (see ether fraction).

Quassin, no characteristic color.

Strophanthin, green, greenish-yellow, brownish-green, finally dirty brown; warmed to 50° to 60°, the green color changes to dark olive, dark brown, violet, dark violet-blue, black with violet tint.

Not a common substance, and not removed to any great extent by $CHCl_3$, most of it remaining in the aqueous solution after the treatment with immiscible solvents.

Santonin, yellow, violet around isolated crystals.

Saponin, yellow, violet shade gradually appears.

Polygalic acid, reddish yellow, gradually red, deep red, and, on warming, dark violet.

Evaporate five to ten drops of the $CHCl_3$ solution,

as before, and treat the residue with one to two drops Froehde's reagent.

Narcein, greenish-brown.
Narcotin, deep green; characteristic.
Hydrastin, sage-green.
Papaverin, purple, gradually blue.
Oxyacanthin, violet changing to yellowish-green on edges.
Saponin, dirty yellow, violet shade develops on edges, changing to indigo blue.
Colchicin, yellow.

Tests of the other substances which were also removed partially by ether, will not be repeated here.

Evaporate five to ten drops of the $CHCl_3$ solvent, as before, and treat the residue with one to two drops of ammonium vanadate.

Narcotin, brick-red, pink in thin layers.
Narcein, reddish-brown.
Papaverin, purple, blue, green, gradually deep blue; characteristic.
Colchicin, yellowish-green.
Hydrastin, pink, bright red, gradually brick-red.
Saponin, violet, purplish-brown; indigo-blue on edges.
Oxyacanthin, dirty violet to reddish-violet.

Evaporate five to ten drops of $CHCl_3$ solution, as before, and treat the residue with one to two drops formaldehyde-sulphuric acid.

Narcotin, purple to slaty, soon fading.

Narcein, deep brown, green on edges, gradually deepening.

Papaverin, purple, violet, crimson; characteristic.

Colchicin, crystals reddish, liquid yellow.

Hydrastin, no reaction.

Evaporate five to ten drops of $CHCl_3$ solution, as before, and treat the residue with one to two drops nitric acid.

Narcotin, deep yellow.

Narcein, yellow fading.

Papaverin, yellow.

Colchicin, deep purple; characteristic.

Hydrastin, yellow.

Geissospermin, purple-red, disappears on heating.

Polygalic acid, ruby-red; on adding more HNO_3 the color becomes brighter, until finally bright yellow.

Perform murexide test for caffein and theobromin. To purify these substances if it is desired to take a melting-point, dissolve in dilute hydrochloric acid, and precipitate with iodine in KI, filter, decompose precipitate with H_2SO_3, shake out with $CHCl_3$ after adding NH_4OH, and determine melting-point of residue. If other alkaloids are present, first precipitate the acid solution with Mayer's reagent, filter, and then add iodine solution to precipitate caffein.

Quassin. Allen's test. Dissolve in $CHCl_3$, shake with Br-water in excess, separate $CHCl_3$ and shake it with NH_4OH. The color due to Br is immediately destroyed, and if quassin be absent both the $CHCl_3$ and NH_4OH will be colorless; in presence of quassin, the

NH_4OH will be colored bright yellow. Substances from Calumba, Colocynth, Cocculus Indicus, and Chiretta do not give any similar reaction. If picric acid is present, it may be removed by shaking the $CHCl_3$ solution with NaOH before adding Br-water.

Chrysarobin. Add dilute or conc. KOH, which forms a red liquid with a green fluorescence.

Fuming HNO_3 gives a red-colored mixture, turning violet on addition of NH_4OH.

On shaking with lime-water, it gives a violet-colored liquid. Chrysophanic acid gives a yellow liquid in both latter tests.

Hydrastin. A solution of the residue in dilute acid gives a precipitate with $K_2Cr_2O_7$, which, on separating, gives a bright red color when moistened with H_2SO_4.

A solution of hydrastin in dilute H_2SO_4 should be treated with a drop of $KMnO_4$. The color of the reagent is immediately discharged, and an intense blue fluorescence develops.

Additional reaction for *hydrastin*, *hydrastinin*, and *narcotin*. A solution of hydrastin 1 : 300 in alcohol, of hydrastinin 1 : 100 in alcohol, and of narcotin 1 : 100, in dilute sulphuric acid and 0.1 c.c. added to 2 c.c. concentrated sulphuric acid will give the following color reactions: With 0.1 c.c. gallic acid 1 : 20 green to blue; with guaiacol or catechol 1 : 20, red tint changing to violet on warming; with morphin, violet. If hydrastin or narcotin be oxidized by acid solution of permanganate, opianic acid is produced, and on adding alcohol until a 1 per cent. solution is obtained, and then treating 0.1 c.c. of this solution with 2 c.c. concentrated sulphuric acid, the following reactions will take place: With 0.1 c.c.

gallic acid a blue color, fading to brown on warming; with guaiacol, red becoming intense blue on warming; with alphanaphthol, gooseberry-red; with betanaphthol, wine-red; with codein in alcohol 1 : 20, violet turning blue on warming.

Hydrastinin hydrochloride solution blackens instantly with Nessler's reagent. Morphin, apomorphin, and picrotoxin precipitate mercury from the reagent.

Gitalin is a new glucoside from digitalis, and is the chief component of commercial digitoxin. It is decomposed by water, ether, and carbon disulphide. The aqueous solution froths on shaking, and is precipitated by tannin. It gives a reducing sugar when boiled with water or alcohol. Sulphuric acid containing ferric chloride produces a violet color. When dissolved in acetic acid, ferric chloride added, and then treated with sulphuric acid containing ferric chloride, the acid becomes indigo-blue, and the zone of contact violet.

The color reactions given with sulphuric acid are usually only characteristic when the substances are pure and alone. Thus if resorcinol is present at the same time as narcein, and had not been entirely removed by ether, a crimson color would appear; or if a trace of tannin were present with hydrastin, narcotin, or narcein, a green color would be obtained. The reaction with resorcinol and sulphuric acid is very characteristic for narcein.

Add sufficient ammonia water to render the acid solution distinctly alkaline, and note the appearances. A green color indicates apomorphin. If the acid solution was red, due to the presence of sanguinarin, the red color

will disappear on the addition of ammonia. If a red color appears on the addition of ammonia, physostigmin is indicated. The following substances will cause a fluorescence: Manaca, sumbul, hydrangea, hydrastin, gelsemium, and pichi, which gives a blue fluorescence with ammonia. Now shake out three times with P.E. Wash the combined solvents with water, filter into a beaker, and evaporate over the steam-bath, using fan. The following substances will be removed: *

Acoin base trace
Aconitin trace 182°–186°, slow heating
Alypin
Aniline
Atropin trace 112°–113°
Benzoylecgonin 90° when hyd., 195° anhyd.
Betaeucain base
Brucin trace 178°
Capsicin
Chelerythrin
Cocain 98°
Conhydrin 118°–121°
Coniin
Emetin trace
Gelsemium bases, small amount
Gujasanol base
Holocain base trace
Hydrastinin 116°–117°
Lupanin
Lycoctonin

* The italics are used to call attention to the commoner substances.

Methylconiin
Nicotin
Novocain base 51°–60°
Peronin base, somewhat
Physostigmin trace
Quinin traces 171°–172° anhyd.
Quinolin
Rubijervin trace
Sanguinarin trace
Spartein trace
Stovain base
Strychnin, partly 265°–269°
Tropacocain 49°
Trimethylamin
Veratrin trace
Yohimbin trace
Pyramidon 106°–107°
Pimento bases
Sarracenia purpurea base
Taraxacum base

Note the appearance of the residue after the solvent is evaporated.

Liquid: Nicotin, spartein, coniin, beta-eucain, gujasanol, physostigmin.

Quinolin, alypin oily.

Coca alkaloids give an oily residue if in small amounts, but if in quantity the cocain crystallizes in the mass.

Amorphous: Antipyrine, brucin, sanguinarin, yohimbin.

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* The italics are used to call attention to the commoner substances.

Hard, colorless, resinous mass: Quinin.

Odor: Tobacco-like, nicotin.

A portion diluted with a little H_2O: Mousy odor, coniin.

Guaiacol-like, Gujasanol.

Pungent, pyramidon odor: Spartein.

Test for alkaloid: Dissolve the residue in P.E., remove five drops, place on watch-glass, and evaporate. Dissolve in one to two drops N/1 H_2SO_4, and add Mayer's reagent. A precipitate indicates an alkaloid. Note the color of this precipitate. If the solution in H_2SO_4 is red, and a red precipitate is obtained, sanguinarin is indicated.

Physiological test: Evaporate ten drops P.E. solution on a watch-glass, concentrating as much as possible in the centre of the glass. If *aconitin* is suspected, perform the test very carefully. Remove a bit on the end of a glass rod and apply it to the end of tongue, rubbing it with the rod. Tingling after one to five minutes indicates aconitin. Bitter indicates *strychnin* and *quinin.* Numbness at once, or after a few minutes, indicates *cocain, beta-eucain, tropacocain, acoin, gujasanol, holocain, novocain, stovain.* Anesthesia is not always obtained with such small quantities, and if no tingling is experienced, indicating aconitin, remove a larger quantity on the end of the finger and rub it thoroughly over the end of the tongue. If no sensation of numbness becomes apparent after five minutes it is doubtful if any of the anesthetics are present. If the residue was oily, evaporate ten drops P.E. solution, and treat with five to ten drops H_2O. Physostigmin will dissolve quite readily. Apply a few drops of this solution to the eye of some

animal having a normally large pupil, and note whether there is any contraction indicating physostigmin.

Evaporate five drops of P.E. solution in a porcelain dish and treat residue with two drops H_2SO_4 containing $K_2Cr_2O_7$. Purple color indicates *strychnin, yohimbin, gelsemium bases.* If coniin is present, an odor of butyric acid will be noted. The change of color in the case of strychnin is purple to cherry-red, gradually fading. Yohimbin gives a purple, but no change like strychnin.

Evaporate five drops of P.E. solution in a porcelain dish, and treat residue with five drops concentrated HNO_3. Red color indicates *brucin, acoin.*

Purple-red to dirty yellow indicates *gelsemium bases.*

Orange color indicates *sanguinarin.*

Yellow soon turning orange, *physostigmin.*

Now evaporate over the steam-bath (if any *antipyrine* is present the mixture will become deep purple on heating with HNO_3), and after the acid is entirely dissipated, as determined by the odor, cool the dish and add five to ten drops alcoholic potassa, noting carefully the odor, and, at the same time, the color produced. An agreeable odor of ethyl benzoate indicates *cocain, aconitin, tropacocain, stovain.* The odor should always be compared with that given by a known residue until the operator is familiar with it. In the case of stovain, the odor of isonitrile is also present. A purple color indicates *antipyrine, strychnin, yohimbin, atropin.* A red color indicates *holocain.*

If no odor develops in the cold, warm slightly over the steam-bath. *Acoin* also gives an agreeable odor, but not that of ethyl benzoate. *Alypin* gives a disagreeable odor.

Evaporate five drops in a porcelain dish and add two drops formaldehyde-sulphuric acid.

A crimson color gradually becoming purple indicates *peronin.* Repeat, using Froehde's solution, and the following color-reactions will be obtained in the presence of peronin: Blue, deep violet, soon fading to dirty brown, then green, and finally slate color.

There are a number of alkaloids which appear in small amounts in this fraction, while the greater portion will be extracted subsequently by ether and $CHCl_3$, and confirmatory tests will give better results when performed on these fractions. This applies to atropin, aconitin, brucin, emetin, holocain, physostigmin, quinin, sanguinarin, spartein, strychnin, and yohimbin.

If the residue consists of crystals apparently pure, determine the melting-point.

In order to purify a residue, dissolve in dilute HCl and precipitate with iodine in KI. Filter and wash with I solution. Dissolve the precipitate in H_2SO_3, pour into separator, add NH_4OH in excess, and shake out with P.E., wash, filter solvent into beaker and evaporate, which will give a residue of pure alkaloid.

Perform several microchemical tests with the residue. Most of the alkaloids give, with certain reagents, precipitates having characteristic forms. This test is most valuable for confirming the identity of an individual. A check should be carried out at the same time with a known sample, until the analyst is familiar with the reactions. The preliminary tests with the color-producing reagents will indicate the alkaloid to be tested for. *Cocain* gives very characteristic precipitates with gold

chlorid, $PdCl_2$, $KMnO_4$, picric acid; and the other anesthetics give characteristic tests.

Coniin and *nicotin* are volatile, and may be separated from the others of this group by boiling in a current of steam. The distillate should be cooled and then shaken out with P.E., and the solvent filtered and evaporated. A portion of this residue on treatment with $AgNO_3$ solution will act as follows: Free coniin gives a brown precipitate of Ag_2O, which afterward becomes black. Nicotin gives a white precipitate, turning dark on exposure to light.

A solution of the residue or of a neutralized acid solution of the residue with $HgCl_2$, gives a white amorphous precipitate with coniin, and a crystalline precipitate with nicotin, both readily soluble in HCl or acetic acid. *Nicotin* and *strychnin* are the only alkaloids giving crystalline precipitates with $HgCl_2$. Strychnin is nearly insoluble in acetic acid. Of course if the residue had been obtained by distillation no strychnin would be present.

A solution of the residue in dilute HCl treated with $PtCl_4$ solution gives a crystalline precipitate with nicotin. Coniin does not give a precipitate unless very concentrated. The $PtCl_4$ compound of nicotin melts at about 275°, darkening at 250°. This should be confirmed with a sample of a known product.

A solution of the residue in dilute HCl treated with picric acid solution gives a precipitate with nicotin, but not with coniin, except in very concentrated solution. Nicotin picrate forms prisms melting at 218°.

Now shake out three times with ether; if ether solution is green, it indicates apomorphine. Wash the com-

bined solvents with water, filter into a beaker, and evaporate over a steam-bath, using a fan. The following substances will be removed: *

Acoin base
Aconitin
Adrenalin, slightly
Anesthesin 89°–91°
Antipyrine 112°–113°
Apomorphin, partly
Apocodein
Atisin from Aconitum heterophyllum
Aspidospermin
Atropin 112°–113°
Bebeerin
Boldin
Brucin 178°
Cannabin
Carpain
Cephaelin 130°
Cevadin
Chelidonin, slightly
Cinchonamin
Cinchonidin trace 200–207°
Cinchonin trace 240–250°
Coca bases not readily sol. in P.E.
Codein 154°–155°
Conessin (Wrightin)
Corydalin
Cuprein 198°

* The italics are used to call attention to the commoner substances.

Cytisin 152°
Delphinin 119°
Dionin base
Emetin
Ephedrin
Ergotinin
Euquinin
Geissospermin 160°
Gelsemin 178°
Gelseminin
Harmalin
Heroin trace 171°
Holocain 121°
Homatropin 98°–99°
Homoarecolin
Hydrastin 132°
Hydrocotarnin
Hydroquebrachin
Hyoscyamin 106°–108°
Jaborin
Jervin trace
Laudanin, slightly
Laudanosin
Lobelin
Methylene Blue
Novocain 51°–60°
Nupharin
Orthoform 141°–143°
Oxyacanthin 210°
Oxyspartein 84°

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* The italics are used to call attention to the commoner substances.

Papaverin 147°
Pereirin
Pelletierin
Peronin base
Physostigmin
Pilocarpin
Pseudaconitin from Aconitum ferox
Pseudopelletierin
Quebrachamin 142°
Quebrachin 214°–216°
Quinidin, sparingly 168°–170°
Quinin 171°–172° anhyd.
Quinolin
Rubijervin trace
Sabadin
Sabadinin trace
Scopolamin 59°
Sanguinarin
Spartein
Strychnin 265°–269°
Suprarenin
Taxin
Thebain 193°
Tritopin 182°
Tropin 61°
Veratralbin
Veratridin
Yohimbin, partly

The tests obtained with the P.E. residue will suggest what to expect in this fraction.

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* The italics are used to call attention to the commoner substances.

If acoin, aconitin, atropin, holocain, physostigmin, quinin, strychnin, sanguinarin, and yohimbin were suspected in the former, they will be found in larger quantities, provided they were present in appreciable amounts in the original material. If the solvent has a magenta shade the presence of apomorphin is strongly indicated.

A blue-colored residue indicates *methylene blue*, this being the fraction where it appears in marked quantity.

A colorless, hard, varnish-like mass, with here and there a crystalline form appearing, indicates *quinin*.

Quinolin gives a liquid residue.

Dissolve the residue in ether and evaporate three to five drops on a watch-glass. Dissolve in two to four drops dilute H_2SO_4, warming, if necessary, and to the solution add a drop of Mayer's reagent. A precipitate shows that alkaloidal substances are present. A red precipitate indicates *sanguinarin*.

Evaporate five drops on a watch-glass, and touch end of tongue to residue, very cautiously at first, and if *aconitin* was indicated in the previous fraction, the test had better be omitted, as a much larger quantity might appear at this point, and this alkaloid is extremely poisonous. If anesthesia is obtained, anesthetics are present. This should be thoroughly established, however, for unless one is familiar with the effect the action of quinin is deceptive.

Evaporate in a porcelain dish. Add two drops concentrated H_2SO_4, and note the color; colorless, with blue color gradually developing, *quebrachin*. Blue indicates *geissospermin*. Red indicates *sanguinarin* and *lobelin*. Pale violet, soon fading, indicates *papaverin*. Yellow

with green fluorescence becoming pale red, finally with a purple tint, most noticeable on rotating or tipping the dish, indicates *sabadin*. Yellow soon becoming blood-red, pink on edges, and then bright red to pinkish-red, indicates *sabadinin*. Yellow, on heating green and finally purple, *pelletierin*. Yellow to purple-red, *atisin*. Yellow with blue fluorescence more noticeable on dilution indicates *quinin* and *euquinin*. Colors are obtained with other alkaloids, but nothing especially characteristic. If no color reaction is obtained, add small crystal $K_2Cr_2O_7$, and rub it around the acid with a glass rod. Purple to cherry-red indicates *strychnin;* purple to green indicates *yohimbin* and *gelseminin*. Blue indicates *quebrachin*.

Evaporate five drops in a porcelain dish. Add two drops concentrated HNO_3, and note the color. Red indicates *brucin* or *acoin*. Orange indicates *sanguinarin*. Purple-red to dirty yellow indicates *gelsemin* and *gelseminin*. Purple-red indicates *geissospermin*, disappears on heating. Yellow soon turning orange, *physostigmin*. Blue to red indicates *orthoform*. Violet to deep mahogany-brown, finally orange, indicates *apomorphin*. Yellow gradually green indicates *heroin*. Yellow solution with crystals orange-red until dissolved indicates *codein*. Pink rapidly disappearing is given by *veratrin* or its allied alkaloids, but not by *sabadin* or *sabadinin*. Now evaporate the acid over the steam-bath and note the residue. A blood-red residue, becoming deep green, is given by *physostigmin*. Blue-green residue indicates *gelsemin*. Red residues are given by *brucin* and *sanguinarin*. Violet on heating is given by *antipyrine*.

When the residue is cool add two to four drops strong

alcoholic KOH, and note the odor and color. *Aconitin* gives a strong odor of ethyl benzoate. Agreeable odors, differing from ethyl benzoate, are given by some of the anesthetics, *acoin*, *subcutin*, while disagreeable odors are given by *alypin*, *holocain*, *novocain*. Benzaldehyde odor is given by *euphthalmin*. *The cinnamyl bases of coca leaves* give an aromatic odor of cinnamic esters. *Orthoform* gives no odor. Purple color indicates *atropin*, *hyoscyamin*, *scopolamin*, *strychnin*, *yohimbin*. *Homatropin does not respond to this test.* Red: *Holocain*, *nirvanin*, *novocain*, *orthoform*, *subcutin* (blood red). The *veratrum* or *sabadilla* alkaloids do not give a characteristic color at this point. With *physostigmin* a brownish-green solution is obtained, a purple color appearing momentarily in thin layers; on subsequently adding acetic acid, the solution becomes green. *Brucin*, if in any quantity, will interfere somewhat with the test.

Evaporate five drops in a porcelain dish and add two drops H_2SO_4 containing formaldehyde. Brilliant violet to purple indicates *codein*, *heroin*, *dionin*. Crimson to purple indicates *peronin*. Deep purple, greenish-blue underneath, gradually deep blue-black, indicates *apomorphin*. Purple, violet to crimson, indicates *papaverin*. Red-brown indicates *thebain*. Dirty black-brown with deep purple gradually developing indicates *apocodein*. Salmon gradually red-brown indicates *subcutin*. Blue fading to yellow indicates *acoin*.

Evaporate five drops in a porcelain dish, and add two drops Froehde's reagent. No color at first, and then gradually blue indicates *codein*. Green, deep green, blue, indicates *dionin*. Purple gradually blue indicates *papaverin*. Crimson purple gradually fading indi-

cates *heroin*. Blue, dirty brown, blue, green-brown, deep purple, with olive shade underneath, noticed on tipping dish, indicates *apocodein*. Blue at moment of solution, deep violet, soon fading to dirty brownish-green, gradually slate-blue, indicates *peronin*. Deep red-brown indicates *thebain*. Yellow, red with violet tinge, indicates *sabadinin*. Pale violet, gray-brown on standing, purplish with yellow on edges, indicates *bebeerin*. Violet changing to yellow and green on edges, *oxyacanthin*. Pale yellowish-pink becoming greenish, on adding HCl greenish-blue, changing to rose with green on edges, ipecac alkaloids *emetin* and *cephælin*. Violet soon fading to brown indicates *physostigmin*. Red changing to green indicates *emetin*. Green indicates *quinin*. *Gelsemium bases* give a magenta color, changed to blue-green by ammonium vanadate; and there are certain of the more commonly occurring alkaloids in this group, which give practically no indication of their presence by the above tests. These include *bebeerin, cevadin, emetin, homatropin, jaborin, pelletierin, pilocarpin, veratridin*.

If *physostigmin* has been indicated, evaporate five to ten drops of the ether solution in a porcelain dish and add 1 c.c. hot NH_4OH. Physostigmin will produce a yellowish-red solution. Evaporate on a water-bath, which will leave finally, on drying, a blue or blue-green residue, which dissolves in alcohol, giving a blue solution. Add excess of acetic acid. which produces a violet-red solution, fluorescent.

If *sanguinarin* is indicated, pour 5 to 10 c.c. of the ether solution into a small flask and pass in slowly HCl gas. If sanguinarin is present, a bright red precipitate of the hydrochlorid will appear.

Microchemical tests should now be resorted to in order to substantiate the presence of certain alkaloids indicated, and for the detection of others not indicated by any of the above tests.

Adrenalin is slightly soluble in ether. A neutralized solution is oxidized by air to oxyadrenalin, and the latter is removed from ammoniacal solution by amyl alcohol, but not by ether, chloroform, or petroleum ether. It gives a bluish-green color with a very dilute solution of potassium ferricyanide containing ferric chloride, and a blue color with ammoniacal solution of phosphomolybdic acid. A solution of adrenalin gives a rose color on addition of iodine, a red color with mercuric chloride, and a reddish-violet with potassium biiodate and phosphoric or iodic acid. A solution of adrenalin (1 : 100000) treated with an equal volume of 1 per cent. sodium nitrate, and then with a few drops of mercuric chloride (1 : 1000), and warmed to 40–50°, gives a rose-red color. Potassium persulphate gives a characteristic red color. These color tests are given by bases closely allied to adrenalin, the aminobase corresponding to adrenalin, dihydroxyphenylethylamine, the corresponding methyl, ethyl, and propyl bases, and aminoacetopyrogallol.

Quinin may be substantiated by the thalleioquin and herapathite tests. Euquinin gives the thalleioquin, but not the herapathite test.

A small quantity of quinine dissolved in 2 c.c. concentrated sulphuric acid and treated with 0.5 c.c. hydrogen peroxide gives an intense yellow color on shaking.

The thalleioquin test is not easy to obtain unless the alkaloid is in considerable quantity, but the following

modifications will be of assistance: Saturated bromine water is added drop by drop until the fluorescence disappears, followed by 10 c.c. alcohol, and then 1 to 2 drops of ammonia; a green color should appear, following the addition of the ammonia, but in dilute solutions it will be very faint; on shaking with chloroform, the green color will be taken up by the solvent and brought into prominence. Salts of quinin should be dissolved in alcohol, and diluted with an equal volume of water before testing. Another modification consists in treating 10 c.c. of a faintly acid aqueous solution with one drop of a mixture of equal parts saturated bromine water and water, followed by one drop 10 per cent. potassium ferrocyanide, and the same amount of 10 per cent. ammonia water, and a shaking with chloroform; a rose color is removed by the solvent.

A neutral solution of the residue should be tested physiologically on a cat's eye. Dilatation is produced by *atropin*, *homatropin*, *hyoscyamin*, *scopolamin*, *gelseminin*, and *gelsemin*. *Euphthalmin* has mydriatic properties. Contraction by *physostigmin* and *pilocarpin*. This test is not always satisfactory for pilocarpin, for the jaborandi alkaloids, under certain conditions, will produce dilatation. Previous color test with HNO_3 and alcoholic KOH will indicate *atropin*, *hyoscyamin*, and *scopolamin*.

Crystalline salts with $PtCl_4$, $AuCl_3$, and picric acid should now be prepared, and their melting-points taken. The aurochlorides of *atropin*, *homatropin*, *hyoscyamin*, and *scopolamin* are characteristic, and should be used for their final identification. The picrate of bebeerin is very characteristic.

Further reactions of certain alkaloids of this group:

Gelsemin: The precipitates formed with gold or platinum chloride are yellow, soluble in hot water, and precipitating in crystalline form on cooling. The pure alkaloids dissolve in HNO_3 to a colorless solution. On evaporating spontaneously a permanent blue-green color is obtained. As usually obtained, gelsemin residues give with HNO_3 yellowish to brownish-green colorations, rapidly changing to deep green. $H_2SO_4+K_2Cr_2O_7$ give reddish-purple to cherry-red, rapidly changing to bluish-green or blue tint. Froehde's reagent—wine-red.

Gelseminin: H_2SO_4 gives a yellow changing to violet with $K_2Cr_2O_7$, and finally green. Its solution causes dilatation of the pupil.

Ipecac alkaloids: A drop of solution of $Ca(OCl)_2$ applied to a fragment of the solid substance, and a drop of acetic acid added, gives a very persistent bright orange or lemon-yellow color. If the solution of $Ca(OCl)_2$ be added to a solution of the alkaloids in dilute HCl, an orange coloration is produced, and a yellow precipitate formed. HNO_3 gives pale orange, brown, changing to bright orange-red. Froehde's reagent, pale yellowish-pink, becoming greenish; on adding HCl, greenish-blue changing to rose with green on edges. A solution in dilute HCl gives a precipitate with $AuCl_3$ on warming. Emetin plantinichloride is amorphous.

Pelletierin: Alkaloid is soluble in 20 parts cold water. No precipitate is given with $PtCl_4$. NH_4OH produces a white precipitate soluble in excess, giving a yellowish-red solution. The tannate reduces $AuCl_3$ to metallic Au.

H_2SO_4 gives yellow, on heating green, and finally purple.

HNO_3 gives no color.

Pilocarpin: Readily soluble in water. Its solutions are dextrorotatory, neutral with litmus, but alkaline to cochineal. $H_2SO_4+K_2Cr_2O_7$ produces a dark green color.

No precipitates formed with tannin, picric acid, or $K_4Fe(CN)_6$. The precipitate with $AuCl_3$ containing 1 molecule H_2O melts at 100°, the anhydrous salt at 138°. 0.01–0.02 gram of a salt of pilocarpin, dissolved in 2 c.c. H_2O, 2 c.c. slightly acid solution H_2O_2 added with 2 c.c. benzol and three to four drops $K_2Cr_2O_7$ solution 1 : 300, and the mixture gently shaken, the benzol will acquire a violet color, blue if the quantity is considerable, while the aqueous layer remains yellow.

In connection with the above test for pilocarpin it should be noted that *antipyrine*, *migrainin*, and *salipyrin* give deep blue. If the peroxide is neutral the tint appears in presence of *pilocarpin*, *pyridin*, and *salipyrin*, but not with *antipyrine* or *migrainin* until acid is added. If the benzol layer is separated and shaken with water faintly acidulated with hydrochloric or sulphuric acid, the aqueous extract will give the color again on addition of peroxide, dichromate and benzol in the case of *pyridin*, *antipyrine*, *migrainin*, and *salipyrin*, but not with *pilocarpin*. *Apomorphin* gives the same test, though the violet is more reddish and the aqueous layer is purplish-red becoming brown-red and brown-green. The reaction may be obtained without peroxide; if the benzol is replaced by amyl alcohol the latter is colored indigo-blue. In both tests the color is changed to green on adding 1 per cent. stannous chloride.

Pilocarpidin: Not precipitated from aqueous solution by $AuCl_3$. The compound with $PtCl_4$ melts at 186°–190°.

Spartein: Three parts of iodine added to an ethereal solution of one part spartein gives a black precipitate. On separating and dissolving in boiling alcohol, green crystalline needles separate on cooling.

Yohimbin reacts as follows: On adding sulphuric acid, a yellow color is obtained which with potassium dichromate gives a purple color changing to blue, red, and finally green; if the amount is large, the first color is indigo-blue, changing rapidly to olive-green. Nitric acid forms a yellow solution which becomes orange on evaporation; alcoholic KOH produces a purple color momentarily, then chocolate, and on warming the residue turns almost black; as the last portion of alcohol evaporates there is an odor of orange flower.

Codein and *dionin* give similar reactions in almost all cases, but with a 10 per cent. solution of codein hydrochloride a precipitate appears on the addition of a few drops of NH_4OH, while dionin dissolves on the addition of 5 c.c. NH_4OH, soon separating on standing, this fact being characteristic with a 1 per cent. solution of dionin.

Aspidospermin with sulphuric acid and lead peroxide gives a brown color changing to purple-red. On boiling with perchloric acid an intense red color results; it is claimed that this reaction is not given when the acid is pure, but only when impurities having oxidizing power are present. Platinic chloride gives a blue precipitate which becomes violet on boiling with excess of the reagent. It forms a yellow chromate which turns green on exposure to air.

Hydroquebrachin gives a violet color with sulphuric

acid, and the same reaction with perchloric acid as aspidospermin. The chloroplatinite is yellow, and dissolves in boiling HCl with a brown-red color, depositing a blue precipitate on standing.

Quebrachin gives a bluish solution with sulphuric acid, turning to blue and brown with dichromate. With perchloric acid the color is yellow.

Quebrachamin gives a violet color with sulphuric acid and bichromate, and a yellow to yellowish-red with perchloric acid.

Aspidospermatin gives with perchloric acid the same color as aspidospermin, but the precipitate with platinic chloride is yellow.

Aspidosamine gives with sulphuric acid a brown color, turning blue with dichromate. With perchloric acid a fuchsine-red color is obtained.

Now shake out three times with chloroform, wash the combined solvents with water, run $CHCl_3$ through cotton into a beaker, and evaporate over the steam-bath, using a fan. The following substances will be removed:*

Aconitin
Atropin 112°–113°
Apomorphine
Berberin trace
Brucin 178°
Cephaelin
Celandin bases
Chelidonin 135°

* The italics are used to call attention to the commoner substances.

Cinchonin 240°–250°
Cinchonidin 200°–207
Codein 154°–155°
Delphinin
Emetin
Heroin 171°
Hydrastin 132°
Hyoscyamin 106°–108°
Isopelletierin
Jervin
Laudanin
Methylene Blue
Morphin trace
Narcein 145° when anhyd.
Papaverin 147°
Pelletierin
Physostigmin
Protopin
Protoveratridin trace
Protoveratrin trace
Pseudojervin
Quebrachin 214°–216°
Quinidin 168°–170°
Rubijervin
Sabadinin
Sanguinarin
Strychnin 265°–269°
Scopolamin
Tritopin
Yohimbin

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* The italics are used to call attention to the commoner substances.

This fraction is in the main used for substantiating certain alkaloids which may have been indicated to a greater or less extent in the previous residues obtained from shaking out the alkaline solutions. *Cinchonin, cinchonidin, yohimbin* will appear at this point in quantities sufficient for their more ready detection than in the previous fraction. *Morphin* will be extracted in small quantity, and *brucin* and *strychnin* are removed by $CHCl_3$ better than by any other solvent.

If atropin, hyoscyamin, scopolamin, codein, heroin, hydrastin, papaverin, physostigmin, sanguinarin, strychnin, or brucin have not been indicated on previous occasions, there is little use of looking for them here. It is well, however, to perform the same series of color reactions as was performed on the ether residue.

Cinchonin and *cinchonidin* give no characteristic color tests.

Morphin gives with HNO_3 a red solution gradually fading, but this reaction is useless when *brucin* is present. With Froehde's reagent and with H_2SO_4 and formaldehyde purple shades are obtained, but morphin is best substantiated in the next fraction.

Aconitin. Dissolve residue in water containing a few drops acetic acid, and take 1 to 2 c.c. in the mouth, rolling it around with the tongue, and then expectorate. If aconitin is present, the peculiar tingling sensation will soon appear. If sufficient alkaloid is present, prepare the aurochlorid, which is a well-defined crystalline salt, wash, dry, and take the melting-point, which, in the case of the pure salt, is 135°.

If *strychnin* is found, and it is desired to test for *atropin, hyoscyamin,* or *scopolamin*, dissolve in dilute

sulphuric acid, add potassium ferrocyanide, filter, add ammonia, and shake out with chloroform; on evaporation the residue will contain the solanum bases free from strychnin, and they may be identified by the michrochemical test, and the preparation of the aurochlorid and determination of its melting-point.

The *cinchona alkaloids* may be separated by the following method, described in Allen: The mixed alkaloids are treated with ether free from alcohol, shaken, and let stand for twelve hours. In solution will be *quinin*, *amorphous alkaloids*, *quinamin*, and traces of *quinidin* and *cinchonidin*. The insoluble portion will contain *cinchonin*, *cinchonidin*, and *quinidin*. Proceed with the examination of the soluble portion as follows: Evaporate, dissolve in ten parts 50 per cent. alcohol, and add one-twentieth of sulphuric acid, add alcoholic solution of iodine so long as a precipitate is produced, avoiding excess. In presence of much *quinin* a black precipitate of herapathite is immediately produced, but if the quantity is small some time is required for its appearance, and in this case only a small amount of iodine must be added, and the liquid well stirred and left twelve hours. The precipitate is filtered and washed with strong alcohol; it may be treated with sulphuric acid and the quinin liberated with ammonia and extracted with ether. The solution containing the excess iodine after filtering from herapathite, is carefully neutralized with NaOH, the alcohol evaporated, excess alkali added, and agitated with chloroform. The chloroform extracts *amorphous alkaloids* with traces of quinidin and cinchonidin; the two latter will remain undissolved on treatment with a limited amount of ether. The amor-

phous bases include quinicin and cinchonicin isomeric with quinin and quinidin, and cinchonin and cinchonidin, respectively, and are present in quinoidin, being formed in the manufacture of quinin. The natural amorphous bases consist of diquinicin and dicinchonicin. *Diquinicin* fluoresces, gives the thalleioquin test, and is dextrorotatory, while *dicinchonicin* does not possess these characteristics. *Quinicin* gives a green color when treated in solution with chlorine- or bromine-water and ammonia, but is distinguished from quinin or quinidin by producing a white amorphous precipitate with sodium or calcium hypochlorite in a liquid slightly acid with hydrochloric acid; it is soluble in sulphuric acid with a yellow color but no fluorescence, and gives no precipitate with Rochelle salt, but is completely precipitated by potassium sulphocyanide, the precipitate being soluble in water, but insoluble in sulphocyanate solutions. *Cinchonicin* closely resembles quinicin, but gives no green color with chlorine- or bromine-water and ammonia. If the neutral oxalates of the amorphous bases be rendered anhydrous by heating at 100°, and the dry salts treated with chloroform, they behave in a characteristic manner; quinicin oxalate dissolves sparingly at the ordinary temperature, but freely on boiling, depositing most of the oxalate in crystals on cooling. The anhydrous cinchonicin oxalate dissolves freely in cold chloroform, and on adding a few drops of water the solution is transformed into a solid mass. The oxalates of the natural bases are very soluble in chloroform, and the solution remains clear on adding a few drops of water, but the water dissolves some of the oxalate from the chloroform.

The cinchona bases which were insoluble in ether are now dissolved in dilute sulphuric acid, the solution exactly neutralized by sodium hydroxide, an excess of a saturated solution of Rochelle salt added, cooled to 15°, and allowed to stand for one hour. If *cinchonidin* is present, crystalline streaks of the tartrate form; the solution is filtered and washed with 5 per cent. solution of Rochelle salt. The filtrate is concentrated to the original bulk, a drop of acetic acid added, and excess of saturated solution of potassium iodide. The mixture is allowed to stand for two hours at 15° with frequent stirring, and if *quinidine* is present, a precipitate of the hydriodide is formed which may be filtered, washed with a little cold water, and the alkaloid recovered by treatment with ammonia. The filtrate is made alkaline with sodium hydroxide, and the cinchonin extracted with chloroform.

The fluorescence of the solutions of cinchona alkaloids has been found to vary; thus when 0.02 gram is dissolved in 2 c.c. glacial acetic acid and 2 c.c. concentrated sulphuric acid, a slight fluorescence is noted with *quinin*, *cuprein*, *cinchonin*, and *cinchonidin;* on adding 0.02 c.c. formaldehyde a strong bluish fluorescence is noted with *quinin* and *cuprein*, with *cinchonin* blue, and *cinchonidin* bluish-violet; on adding 3–4 c.c. water the fluorescence of the cuprein disappears and the green of the quinin is accentuated; on further dilution with water the fluorescence of cinchonidin disappears rapidly, and is barely visible at 10–15 c.c., while it is evident up to 50 c.c. with quinin, and stronger still with cinchonin.

Shake out three times with a mixture of chloroform and alcohol, 2 : 1, filter solvent, and evaporate over steam-bath using fan. The following substances will be removed: *

Berberin
Narcein 145° when anhydrous
Morphin 254° rapid heating
Solanin
Salicin 200°–202°
Strophanthin

Note whether residue is crystalline. *Morphin*, if present in sufficient quantity, will appear in crystalline condition. Note color; *berberin* will give a yellow residue.

Dissolve the residue in a mixture of $CHCl_3+C_2H_5OH$ (2 : 1), or dissolve in alcohol and add twice the volume of $CHCl_3$.

Evaporate 1 to 2 drops on a watch-glass. Dissolve residue in 2 to 3 drops dilute H_2SO_4, and add Mayer's reagent. A precipitate shows the presence of an alkaloid.

Evaporate 2 to 4 drops in a porcelain dish and add 1 to 2 drops concentrated H_2SO_4. Red color indicates *salicin*. Deep brown at moment of solution, yellowish gradually becoming green, and finally blue, indicates *narcein*. Orange, olive-green on warming, indicates *berberin*. Add a crystal of $K_2Cr_2O_7$, and note reaction. With *berberin* a violet shade, becoming brownish-green, will be observed. There are many descriptions of this reaction, probably due to the condition in which it occurs as extracted from the extract of the drug.

* The italics are used to call attention to the commoner substances.

Evaporate 2 to 4 drops in a porcelain dish, and add 1 to 2 drops concentrated HNO_3. Deep red, gradually fading, indicates *morphin*. *Berberin* gives a dark reddish-brown liquid, which, on dilution with H_2O, gives a yellow precipitate partly soluble in NH_4OH.

Evaporate 2 to 4 drops in a porcelain dish and add 1 to 2 drops Froehde's reagent. Purple coloration is given by *morphin* and *salicin;* greenish-brown fading indicates *narcein;* greenish-brown to dark brown or violet indicates *berberin*.

Evaporate 2 to 4 drops in a porcelain dish and add 1 to 2 drops formaldehyde-sulphuric acid. Deep purple indicates *morphin*.

Salicin when subjected to hydrolysis with dilute acid, using a reflux, is hydrolyzed, giving *saligenin*. The solution should be shaken out with ether, and the ether filtered and evaporated, which leaves the *saligenin*. An aqueous solution of this product is colored indigo-blue by $FeCl_3$. The residue is soluble in concentrated H_2SO_4 with a bluish-red color.

Morphin should be crystallized out and its melting-point determined.

STILL IN SOLUTION *

Adonidin	*Convallamarin*
Arbutin	Cnicin
Aloin	Curarin
Berberin	Cyclamin
Cellotropin	Dulcamarin
Bryonin	Ergotic Acid

* The italics are used to call attention to the commoner substances.

Gentiopicrin	Protoveratridin
Gentiamarin	Senegin
Helleborein	Saponins
Hexamethylenetetramin	Sapotoxin
Narcein	Sarcosin
Ouabain	Senecin
Phenolsulphonic Acid	Sozolic Acid
Pinipicrin	(Orthophenolsulphonic)
Polygalic Acid	Tannic Acid
Protoveratrin	Thujin
Glycerin	

Salts soluble both in water and alcohol; see table No. 1

From the table above it will be noted that there are a number of fairly common organic substances which are not removed by the regular group solvents. In certain instances it will be found difficult to identify their presence with any degree of certainty, though often, if the possibility of an individual is suspected, it may be substantiated by taking a fresh portion of the original substance. The following paragraphs describe some of the characteristic reactions of these substances by no set scheme of separation. The procedure depends on the particular product involved, and must be left to the judgment of the worker.

The solution may be rendered slightly acid, and shaken out with washed and redistilled ethyl acetate, in order to remove arbutin and tannic acids; dilute ferric chloride gives with an aqueous solution of the former a fine blue color, and a green or black color with the

* The italics are used to call attention to the commoner substances.

tannic acids. The gentian glucosides are also removed by this treatment.

Arbutin gives a blue tint when treated with a solution of sodium phosphomolybdate in hydrochloric acid followed by a slight excess of ammonia. A 1 per cent. solution reduces ammoniacal silver nitrate on boiling, and gives a precipitate with sodium hypobromite. On boiling with dilute acids, quinol or hydroquinone is formed; the latter is readily removed from acid solution by ether, and its production under these conditions indicates the presence of arbutin; it may be identified by its melting-point, 169°, sublimation on heating, its precipitating Fehling's and ammoniacal silver nitrate solutions, and the sodium hypobromite color reaction.

Some of the tannins yield phenolic substances on boiling with mineral acids, but the chemistry of these substances in relation to pharmaceutical chemistry is in its pioneer stage. In general, one should draw no conclusions relative to the identification of arbutin unless the absence of tannins has been assured, or they have been removed by precipitation with lead salts or magnesium hydroxide.

Hexamethylenetetramin. This substance is very soluble in water, and is not removed to any great extent from either acid or alkaline solution by immiscible solvents. It gives a heavy precipitate with Mayer's reagent, hence, if after removing all other bases by immiscible solvents, the solution on acidifying gives a precipitate with Mayer's reagent, the presence of this body may be suspected. An aqueous solution gives a precipitate with mercuric chloride which may be separated and treated with dilute mineral acid in a distilling flask. On boiling,

formaldehyde and ammonia are formed. The distillate may be tested for formaldehyde by the reverse of the codein or morphin reaction; it is made alkaline with magnesia and redistilled, collecting a small quantity of the distillate in a tube containing ammonia; the excess of ammonia is evaporated under reduced pressure over sulphuric acid, the residue dissolved in 0.5 c.c. water, a drop of ammonia added and evaporated over the water-bath; when cold, sulphuric acid containing codein or morphin is added, and the color compared with that obtained with a pure crystal of hexamethylenetetramin.

Saponins. These substances compose another group whose chemistry is yet in the pioneer state so far as our work is concerned, and in searching for them one had better work with a portion of the original mixture. Their presence will often be evident long before they are actually separated, and if in considerable quantity will sometimes prevent satisfactory shaking out with immiscible solvents.

Neutral saponins are precipitated by lead acetate, and acid saponins by lead subacetate; most of them are precipitated by barium hydroxide. From a plant decoction the tannins and coloring matter may first be removed by magnesium hydroxide.

To detect saponin, neutralize with magnesium carbonate, add 20 grams ammonium sulphate and 10 c.c. phenol; after shaking, the phenol solution is separated and shaken with 50 c.c. water and 100 c.c. ether, with the addition of alcohol if necessary to prevent emulsification; the aqueous layer may be drawn off and allowed to dry in a desiccator. The contents may be digested

with acetone, and after this has been decanted the residue tested for saponin. Sulphuric acid gives a red to violet color on warming, the solution sometimes becoming fluorescent. Froehde's reagent gives a purplish shade, and a solution in water froths on shaking, this property being interfered with by acids or alcohol. They differ in regard to their solubility in water, some being easily dissolved by cold water, others by water containing alkali, and still others are insoluble unless the liquid contains a water-soluble or an impure saponin.

An aqueous solution of many saponins reduces gold chloride, ammoniacal silver nitrate, potassium ferricyanide, ferric chloride, and mercuric chloride and permanganate.

If dextrin is present, the liquid should be concentrated to 20 c.c., and precipitated with 150 c.c. of 95 per cent. alcohol; after standing thirty minutes, the mixture is boiled on the water-bath, filtered, the alcohol removed by distillation, the solution diluted to 100 c.c., and then treated as above.

An aqueous solution of a saponin on boiling with a mineral acid yields glucose and a variety of other products, depending on the saponin used, and known as sapogenins and endsapogenins.

The Gentian Glucosides. Gentian may be dried in the air under cover without losing much gentiopicrin, but this glucoside is usually in small amount in the commercial drug; it is also hydrolyzed by alcohol, and the ordinary medicinal preparations are therefore free from it. Gentiopicrin is soluble in ethyl acetate, and the crystals have a melting-point 189°, and a strong levo-rotation; gentiogenin is produced on hydrolysis, and

gives with sulphuric acid a brown color, changing to blue with water.

A carefully prepared dialyzed extract of the fresh root in 60 per cent. alcohol contains both glucosides, gentiopicrin and gentiamarin; it is fluorescent, and from it both glucosides may be removed by ethyl acetate.

Eupatorium glucosides, eupatorin and rebaudin, are sweet principles soluble in water, and not removed by immiscible solvents, or precipitated by acids.

Eupatorin is soluble in absolute alcohol, but rebaudin is not; they are both levorotatory.

Strophanthin is readily changed by mineral acids even in the cold to glucose and strophanthidin, or by heating at 70° for one hour with dilute sulphuric acid. Strophanthidin is slightly soluble in cold water, but readily soluble in chloroform, and may be removed by shaking with this solvent.

An aqueous solution of strophanthin froths on shaking. It is not precipitated by neutral or basic lead acetate, but an aqueous solution of the drug gives a precipitate due to kombic acid; it is precipitated by tannin, the precipitate dissolving on agitation, until an excess is added. With phosphomolybdic acid the solution gives a green color, gradually changing to greenish-blue. Pure strophanthin gives a green color with sulphuric acid, rapidly changing to greenish-yellow and brownish-green, and in an hour or two becoming dirty brown without any green; when moistened with sulphuric acid, and heated to 50–60°, the green color becomes dark olive changing to very dark brown, then violet and dark violet-blue, and finally to black with violet tint. With dilute sulphuric acid, it gives a nearly colorless solution, developing

various shades of green on heating to 50°, and changing to violet, and in about two hours to violet-black. Ten per cent. nitric acid dissolves strophanthin without color; but on heating to 50° a violet color appears, changing gradually to yellowish-brown, and finally to gamboge-yellow.

The aqueous solution which was originally set aside should now be examined for tannates, lactates, lacto-phosphates, citrates, acetates, valerates, sulphocarbolates, tartrates, sulphites, hyphophosphites, glycero-phosphates, and thiosulphates, using about one-half the volume. Then evaporate the balance, ignite cautiously, and perform basic and acid analyses according to some approved scheme.

Tannic acid may be identified by precipitating the solution with lead, filtering, and washing precipitate and decomposing it with hydrogen sulphide in the presence of alcohol, to which a trace of ammonia is added. On filtering and evaporating the acid will be left in the form of its ammonium salt, and may be identified. This same procedure will also serve to detect citric and tartaric acids.

Glycerin may be detected by evaporating the solution in the presence of milk-of-lime, extracting the residue with absolute alcohol, filtering, and adding two volumes of absolute ether. After standing until the precipitate has settled, the supernatant liquid is filtered and evaporated, and the residue tested qualitatively for glycerin. It is advisable to use the solution from which the various principles have been removed by immiscible solvents, as their presence might interfere with the glycerin reactions.

Mulliken's test for glycerin is as follows: The residue is diluted with water to about 1 per cent. treated with 5 drops of 1 per cent. solution pyrogallic acid and 3 c.c. sulphuric acid, and boiled for about half a minute, when in the presence of glycerin a purple color begins to develop. On cooling and adding 20 c.c. alcohol, the color shows to advantage.

To perform Denigé's tests for glycerin, about 0.2 gram of the residue is heated for twenty minutes on a water-bath with 10 c.c. bromine water, and then boiled until the bromine is expelled. 0.2 c.c. of this solution is treated with 0.1 c.c. alcoholic 5 per cent. solution of codein, 2 c.c. water, and 2 c.c. sulphuric acid, and heated in a water-bath, when a greenish-blue color will be observed. 0.4 c.c. portions of the same solution are treated respectively with 0.1 c.c. alcoholic solutions of resorcinol, thymol, 5 per cent. each, and betanaphthol 2 per cent., and 2 c.c. sulphuric acid; in the cold the resorcinol gives a blood-red color, and the thymol a wine-red color, changing to rose on dilution; with the betanaphthol an emerald green with a greenish fluorescence appears on warming.

2. Substances Soluble in Alcohol, but Insoluble in Water

Most of the resins will appear at this point. Treat the residue with ether, filter into a separator, and shake out with normal sulphuric acid; separate the acid, add ammonia, shake out with ether, filter, and evaporate solvent, examining the residue for cocain or other alkaloids. Then shake out the original ether solution with

dilute alkali, separating the alkali and reserving the ethereal solution.

To the alkaline solution add dilute sulphuric acid in slight excess and shake out with ether, wash ether with water, and then filter and evaporate. The residue will contain the resin constituents soluble in alkali, fatty acids, salicylic and benzoic acids, phenolphthalein, and others. Many resins have characteristic odors which will indicate their identity, and below is given a brief summary of their chief characteristics.

Ammoniac contains about 60 per cent. of resin soluble in ether, and a portion of this is acid resin which is removed by alkali. It contains ammoresinotannol united to salicylic, butyric, and isovaleric acids, which latter may be obtained on saponification. Ammoniac also contains a portion of gum.

African ammoniac consists of about 68 per cent. resin, 9 per cent. gum, 19 per cent. bassorin and other substances, and 4 per cent. of water and oil.

Asafetida has a characteristic odor, and consists of about 62 per cent. of the ferulic acid ester of asaresinotannol, less than 1 per cent. of free asaresinotannol, 25 per cent. of gum, from 6 to 7 per cent. of ethereal oil, 1 to 1.5 per cent. ferulic acid, 2.3 per cent. water, and a trace of vanillin. Ferulic acid on fusion with KOH yields resorcin and protocatechuic acid.

Aloe Resin. Barbadoes aloes contains a cinnamic acid ester of aloeresinotannol.

Cape aloes contain the *p*-cumaric acid ester of aloeresinotannol.

Natal Resin contains the *p*-cumaric acid ester of nat-

aloresinotannol. On saponification the resinotannol is obtained as an aromatic powder soluble in alkalies.

Bryony Resin, dark brown, viscid, contains bryonol, a dihydric alcohol m 210–212°, and yielding a diacetyl deriv. m 152°

Benzoin. Siam benzoin contains only benzoic acid. Sumatra benzoin contains cinnamic and benzoic acids. Singapore benzoin contains cinnamic and benzoic acid. Sumatra benzoin contains vanillin, cinnamic acid-phenylpropylester and styracin, cinnamic acid united with resinotannol, and a little benzoresinol. Siam benzoin contains the benzoic ester of benzoresinol and siaresinotannol.

Canada Balsam. This contains 24 per cent. of a levo-terpene, $C_{10}H_{16}$, boiling at 167°, and giving with hydrochloric acid a crystalline compound; 13 per cent. canadinic acid soluble in ammonium carbonate, 0.3 per cent. canadolic acid, 50 per cent. alpha- and beta-canadinolic acids, 24 per cent. ethereal oil, 12 per cent. canadoresene. Acid No. 82 to 86; sapon. value cold 94, hot 197. Alpha-canadinolic acid is soluble in ordinary solvents, gives the cholesterin reaction, and is precipitated by alcoholic lead acetate. Beta-canadinolic acid is not precipitated by alcoholic lead acetate.

Cascarilla.

Cimicifuga.

Copaiba. Consists of volatile oil, copaivic acid, and a resin. Betametacopaivic acid gives the Liebermann cholesterin reaction, and in the Salkowski-Hesse reaction the chloroform remains colorless, with sulphuric acid yellow without fluorescence. Para- and homo-copaivic acids give orange to green in the Liebermann

test, and the same as the beta acid with the Salkowski-Hesse test. Illurinic acid gives with the Liebermann test orange, red, purple-green.

Colocynth. The resinous portion contains alpha-elaterin melting 232°.

Cusso. The resin is soluble in alkali.

Damiana. The resin is dark green in color, and has a characteristic odor.

Gamboge. Soluble in alkali.

Eriodictyon (Yerba Santa). The resin is soluble in alkali.

Galbanum. Contains 10 to 20 per cent. volatile oil, 50 to 67 per cent. resin, and 15 to 20 per cent. gum. The resin is soluble in ether and alkalies, contains 0.25 per cent. free umbelliferon and 20 per cent. umbelliferon combined with galbano-resinotannol. On dry distillation it yields a blue oil having the odor of chamomile; on fusion with KOH it yields resorcin and an acid. It gives a blue color with ammonia.

Grindelia Robusta.

Guaiac. The resin is soluble in alcohol and alkalies, and turns blue with oxidizing agents.

Ipomœa Resin. Analysis has shown this resin to contain 8 per cent. substance soluble in petroleum ether, which fraction on treatment with alcoholic KOH yielded pentatriacontane, a phytosterol melting 132–133°, formic, butyric, stearic, palmitic, and higher volatile acids; 7.3 per cent. soluble in ether, yielding azelaic acid in addition to the above; 9.8 per cent. soluble in chloroform; 23.8 per cent. soluble in ethyl acetate, yielding ipuranol melting 285–290°, whose acetyl derivative melts 160°, and other products of acid nature; and 50 per cent.

soluble in alcohol yielding ipurolic acid melting 100–101°.

Jalap Resin. This body has been the subject of an extended research by Power and Rogerson. They fractionated the resin with volatile solvents, and reported as follows: 1.9 per cent. soluble in petroleum ether containing free palmitic and stearic acids, and yielding on hydrolysis formic, butyric, higher volatile acids, palmitic acid, linolic and other unsaturated acids, a phytosterol, and another substance resembling a phytosterol melting 56–57°; 9.7 per cent. soluble in ether yielding ipurganol melting 222–225°, a substance with color reactions similar to the phytosterols, and giving a diacetyl derivative melting 166–167°; on hydrolysis this fraction gave cetyl alcohol, volatile acids, phytosterol, and amorphous products; 24.1 per cent. soluble in chloroform yielding beta-methylesculetin, and on treatment with alkalies and sulphuric acid formic, butyric, convolvulinolic, and *d*-methyl-ethyl acetic acid, and glucose; 22 per cent. soluble in ethyl acetate, the fraction yielding the same acids on hydrolysis; 38.8 per cent. soluble in alcohol melting at 150–160° after charcoal purification, and levorotatory; KOH fusion gave formic, acetic, butyric, valeric and higher volatile acids, azelaic and sebacic acids; hydrolysis with barium hydroxide gave *d*-methyl-ethyl acetic acid, and an amorphous product soluble in water called the "hydrolyzed resin." The latter on systematic examination yielded the same acids as above, and in addition ipurolic acid.

Asiatic Scammony (Convolvulus scammonia) has saponification value 179–229, acid number 14–28. Mexican scammony (Ipomœa orizabensis) has saponification

value 180–185, acid number 14–15. Taylor shows that pure scammony resin from both sources is soluble in ether, 96–97 per cent. true resin, having saponification value above 230, while that of the Mexican is between 185 and 200.

Gelsemium Resin amounts to 3 per cent. of the drug, and contains pentatriacontane, ipuranol, emodin monomethyl ether, and a phytosterol.

Leptandra Resin amounts to 6–7 per cent. of the drug, yielding a phytosterol melting 135–136°, acetyl derivative melting 119–120°, and on hydrolysis oleic, linolic, palmitic, stearic, paramethoxycinnamic, and 3.4-dimethoxycinnamic acids.

Gurgun Balsam contains a terpene, gurjunic acid, and resin.

Fabiana Imbricata (pichi). The resin contains fabianeresene which is soluble in ether and sublimes. On treatment with sulphuric acid it turns yellow, and the solution becomes red on warming. On adding water to this solution a colorless amorphous precipitate is obtained. Its solution in phenol is colored yellow-brown on heating with zinc chloride, and on adding sulphuric acid a rose-red color appears, soon changing to purple.

Jalap. The resin is soluble in alkali.

Kamala. The resin is soluble in alkali.

Mastic is soluble in alkali.

Myrrh contains 67 to 75 per cent. gum, resin, and two acids. On treating 6 drops of a solution of bisabol myrrh in petroleum ether with 3 c.c. glacial acetic acid and 3 c.c. concentrated sulphuric acid, a rose-red zone appears which is quickly communicated to the acetic

acid portion. Herabol myrrh gives a green zone and a red acetic acid portion.

Olibanum contains 72 per cent. resin soluble in alcohol, and 28 per cent. insoluble. The former contains 33 per cent. boswellinic acid, 1.5 per cent. of the acid combined as ester, 33 per cent. olibanoresene, 4 to 7 per cent. of terpenes, and 0.5 per cent. bitter substance; the latter contains 20 per cent. gum, 6 to 8 per cent. bassorin, and 2 to 4 per cent. plant residue. Olibanoresene is soluble in organic solvents and insoluble in alkalies. Boswellinic acid has a melting-point of 150°. It forms a blue salt with copper.

Opoponax consists of 51.8 per cent. ether-soluble resin (ferulic acid ester of oporesinotannol), 1.9 per cent. ether insoluble resin, 33.8 per cent. gum, 8.3 per cent. ethereal oil, and small quantities of ferulic acid. Oporesinoltannol is soluble in alcohol, alkalies, chloroform, glacial acetic acid, acetone, and slightly soluble in ether, ammonia, toluol, and carbon disulphide, and insoluble in petroleum ether. On treatment with nitric acid, nitrous fumes are evolved, and oxalic and picric acids are formed.

Peru Balsam consists largely of benzyl benzoate, a colorless oil, free vanillin, free cinnamic acid, and a resin consisting of the benzoic- and cinnamic-acid esters of peruresinotannol. Cinnamein or peru balsam oil, the oily liquid separating on agitation with alkali, contains benzyl benzoate, benzyl cinnamate, benzyl alcohol, and other aromatic compounds.

Podophyllum.

Sandarac contains the hydrocarbon *d*-pinene, and a diterpene and *i*-pimaric and callitrolic acids.

Scammony is soluble in alkali.

Storax contains cinnamic acid, styrol, styracin (cinnamyl or styrylcinnamate), cinnamic acid-ethyl ester, cinnamic acid-phenylpropyl ester, and storesinol; the latter is soluble in alkalies and on distillation gives phenol, cresol, benzol, and toluol; on oxidation with permanganate it yields phthalic acid, benzoic acid, and an acid insoluble in water.

Taraxacum.

Tolu Balsam. Consists largely of a resin which is a combination of tolu resinotannol with cinnamic acid, and a small amount of benzoic acid. It also contains an acid aromatic oily liquid chiefly benzyl benzoate, with a little benzyl cinnamate, about 20 per cent. of free cinnamic acid, and small quantities of a volatile oil and vanillin.

CHARACTERISTICS OF AROMATIC BALSAMS TOLU, PERU, AND QUINO-QUINO, ALL YIELDED BY SAME TREE BUT FROM DISTINCT BOTANICAL VARIETIES.

	Tolu.	Peru.	Quino-quino.
Acid value....	114–158	68–80	80.3
Saponification value.......	155–187	Over 245	134
Ester value....	Up to 73	At least 165	53–54
Cinnamein....	7.5%	62–64%	5–6%
Benzyl benzoate in cinnamein	Present in quantity	Almost wholly	Almost exclusively
Benzyl cinnamate in cinnamein	In small amount	Very small amount	Only traces
Vanillin......	0.05%	0.046–0.05%	0.04%
Free benzoic acid	Small amount	None	In greater part

CHARACTERISTICS OF AROMATIC BALSAMS TOLU—(Continued).

	Tolu.	Peru.	Quino-quino.
Free cinnamic acid	The greater part	Exclusively	In minute amount
Resin.........	80%	30%	78.5%
Free resin alcohol.......	None	None	5–6%
Resinotannol	Toluresinotannol	Peruresinotannol	Toluresinotannol
Benzoic acid in resin	Small amount	Very small amount	All
Cinnamic acid in resin	In predom. quantity	In predom. quantity	None

The ethereal solution should now be evaporated and the residue examined for cantharidin, iodoform, mercuric iodide, phosphorus, sulphur, etc.

MELTING POINTS OF AUROCHLORIDES, PLATINOCHLORIDES, AND PICRATES

	Aurochloride.	Platinochloride.	Picrate.
Atropin	135–138°	207–208° with decomp.	
Hyoscyamin.	160–162°	206° with decomp.	161–164°
Scopolamin..	198–199° When anhyd. 214°		187–188°
Homatropin .	142–145°		
Aconitin....	135.5° when crystallin.		
Cusparin....	190°	179°	
Cusparidin..	167° (?)	182° (?)	
Galipin	174–175° (?)	174–175° (?)	
Galipidin....	167° (?)	182° (?)	
Atisin......		229° with decomp.	
Chelerythrin.	233° with decomp.		
Corydalin. ..	207°		
Pilocarpidin .	125–128°	Anhyd. 186–190° with decomp.	
Isopilocarpin	158–159°, on boiling with H_2O gives comp. 185 to 186°	222–227°	

MELTING POINTS OF AUROCHLORIDES—(Continued).

	Aurochloride.	Platinochloride.	Picrate.
Pilocarpin...	117–130°, on boiling with water gives comp. 163-167°	213–218° with decomp.	
Cevadin.....	182°		
Anhalonidin.	152°		
Japaconitin..	Needles out of alcohol 231°; prisms out of chloroform 154–160°		

3. SUBSTANCES INSOLUBLE IN ALCOHOL, BUT SOLUBLE IN WATER

This fraction will contain sucrose if it was present in any quantity, and many salts of organic and inorganic acids. A portion should first be tested for acids which are altered by heat as described under the first fraction, special tests performed for the few organic bodies liable to be present, and then the balance ignited cautiously, and the residue tested for bases and acids.

Proteins. Five c.c. of the solution to be tested are mixed with a few drops of formaldehyde, a trace of dilute ferric chloride added, and the mixture overlaid on sulphuric acid in a test tube; if proteins are present a violet ring appears at the junction.

If 1–2 c.c. of the solution are treated with 2–4 drops of a 5 per cent. solution of sodium nitroprusside, and then a few drops of ammonia, a purple red color appears, destroyed by acetic acid.

A similar reaction may be obtained with a precipitate obtained by means of ammonium, magnesium, or sodium

sulphate, phosphotungstic acid, or alcohol. The precipitate is washed, placed on a piece of porous paper moistened with a few drops of nitroprusside and ammonia added, whereupon a purple-red color appears.

4. Substances Insoluble in Alcohol and Water

In this fraction we will meet with starch, calcium carbonate, and siliceous material, and other substances used as diluents in the making of pills and tablets. There will be present but few organic active principles except possibly some cantharidin, iodoform, and a few of the compounds of organic substances and bases which can be determined from the table. Starch is readily detected. Bismuth subgallate is soluble in alkali to a yellow solution, and giving a black sulphide on treatment with hydrogen sulphide, in which the metal can be identified by separating and making appropriate tests. The citrate will also dissolve in alkali.

The residue should then be treated successively with hydrochloric acid, nitric acid, and aqua regia, and each solution examined according to the regular procedure for basic and acid analysis. In drug products the active ingredients will hardly be other than those given in the tables, and the solubility tables given in standard textbooks of qualitative analysis will show any other possibilities.

All medicinal preparations should be examined for arsenic, the tests being carried out on a fresh sample, and not from that employed in the previously described separation. The product should be digested first with nitric acid, then evaporated, treated with sulphuric acid,

ST				
…mat …$_2$SO		…ride to …lution	Potassium Permanganate	A. Bromine Water B. After addition of ammonia
i o		......	Immeditate reduction. Precipitate dissolves.	A. Dirty yellow curdy precipitate. B. Purple precipitate sol. in $CuCd_2$.
ucti	.	......	....	A. —— B. White precipitate.
ple. n.	.	......	Immediate reduction, brown color	A. White precipitate. B. No change.
ctio	.	......	....	A. Yellow precipitate. B. White precipitate.
to	.	......	....	A. —— B. ——
ctio		......	Reduction.	A. Yellow milky precipitate. B. Brown-gray precipitate.
luc gre	n	ple col-	Immediate reduction.	A. Yellow precipitate. B. Sol. to yellow solution.
...	.	......	Reduction to clear brown-red sol.	A. Bright yellow precipitate. B. White precipitate.
blue			Reduction to green precipitate.	A. Yellow-green precipitate.
.	..	......	....	A. Precipitate white. B. No change.
...	.	......	Green at once.	A. White precipitate. B. No change.
irty		......	Dilute permangan. is immediately decolorized, and when excess is added reduction.	A. White precipitate. B. No change.

Color Reactions of the Opium Base

	Froehde's.	Ammonium Vanadate.	Formaldehy
Morphin.......	Purple, fading to slate.	Yellow—faint violet—dirty brown—slate.	Deep pur
Codein........	No color at first, gradually blue.	Pale green—gradually blue.	Deep pur
Heroin........	Crimson - purple, soon fading.	Pale violet, soon fading.	Crimson deepeni
Dionin........	Gradually green—deep green—*blue.*	Gradually green.	Yellow-pu ening.
Apomorphin....	Deep blue, fading to slaty-violet.	Deep blue.	Purple — blue un finally c black.
Peronin........	Brown — violet — dirty brown-green—slate.	Olive brown.	Crimson purplish
Narcotin.......	Deep green.	Brick-red—pink in thin layers.	Purple t soon fad
Narcein........	Green-brown, fades.	Reddish brown.	Brown, g edges, deepeni
Papaverin......	Purple, gradually blue.	Purple — blue — green—deep blue.	Purple — crimson
Thebain........	Red brown.	Red brown.	Red brow
Apocodein.....	Blue — dirty brown — blue - green — purple—olive underneath.		Brown - brown—
Hydrastin.....	No reaction at first, gradually deep green.	Pink—bright red—brick red.	No reactio
Colchicin.......	Yellow.	Yellowish-green.	Crystals r quid yel

AND DERIVATIVES AND OTHER ALKALOIDS

$\cdot H_2SO_4$.	$K_2Cr_2O_7+H_2SO_4$.	H_2SO_4.	Nitric Acid.
	Greenish - gray — dirty green.		Deep red, gradually fades.
	Dirty green.		Yellow, crystals orange until dissolved.
urple,	Flesh color momentarily.		Pale yellow, gradually *green*.
, deep-	Greenish-yellow.		Yellow.
eenish neath, blue-	Deep green.		Violet, mahogany, brown, orange.
dually it.	Yellow brown.		Yellow.
slate, .	Pink — brick red — reddish-yellow — pink in thin layers.	Pale yellow — pink on edges — red gradually develops.	Deep yellow.
n on dually		Brown — yellow — green — finally blue.	Yellow fading.
let —	Purple — brown — finally purple.	Pale violet soon fading.	Yellow.
	Red brown.		Yellow.
ck — rple.			
	Brown — pinkish-violet — brown.	No reaction.	Yellow.
ish, li- r.	Green soon fading.		Deep purple.

heated until well charred, more nitric acid added, again heated, and this procedure repeated until the final solution is nearly colorless and all nitrous fumes are driven off. This solution may then be introduced directly into the Marsh apparatus or subjected to any reliable test approved by the analyst.

Tables of the reactions given by the opium alkaloids and by cocain and other local anesthetics.

SECOND PORTION

As explained in the introduction, the second portion of this work describes the methods to be employed in manipulating the various classes of medicinal products in order to effect a separation of their constituents according to the preceding scheme.

These products may be roughly divided into three groups—liquids, solids, semi-solids and oily preparations. Under these groups the classes naturally fall as follows:

Liquids

1. Fluidextracts and plain tinctures.
2. Elixirs, glyceroles, wines, cordials, liquors, bitters, vinegars, and syrups.
3. Emulsions.
4. Liniments.
5. Toothwashes and gargles.

Solids

1. Powdered extracts, solid extracts, and concentrations.
2. Pills, tablets, lozenges, troches, and pastilles.
3. Powders, cachets, hard capsules, and dusting powders.
4. Globules and soft capsules.
5. Granular preparations and artificial mineral-water salts.

Semi-solids and Oily Preparations

1. Pastes, ointments, and emollients.
2. Inhalants.
3. Suppositories, crayons, and bougies.
4. Plasters.

Following this is a chapter devoted to the examination of galenical products for digestive properties.

FLUID EXTRACTS AND PLAIN TINCTURES

Little need be said with reference to this class; as a general thing a sample will contain the extractive matter and active principles of but a single drug, and an examination will follow the procedure prescribed for separating those substances which are soluble in water and alcohol. A preliminary manipulation, if necessary, should follow the lines laid down in the following class which describes the procedure to be observed with liquids in general.

ELIXIRS, ETC.

Divided into two subdivisions, those containing sugar, and those without.

With Sugar	*Without Sugar*
Elixirs	Glyceroles or Glycerites
Syrups	Liquors
Cordials	Bitters
Wines	Decoctions
	Infusions

Liquid tonics, cough mixtures, headache mixtures will fall under one or the other of the above subdivisions.

Elixirs are aromatic, sweetened, spirituous preparations of medicinal substances, containing a large percentage of sugar. They may contain almost anything in the category of medicine.

A *cordial* is practically the same as an elixir.

A *syrup* is very much the same as an elixir, but without alcohol.

Medicinal wines are solutions of medicinal substances in wine, usually fortified with alcohol, and often with added sugar. They contain, in general, little else than vegetable principles, or albuminous substances as beef extract, with occasionally iron and antimony.

Glyceroles are solutions of medicinal substances in glycerin. Pepsin, hydriodic acid, hypophosphites, heroin, and some others are often administered in this form.

Liquors or *solutions* are solutions of medicinal substances, sometimes containing alcohol or glycerin, but no sugar. A great many substances, both organic and inorganic, may be present.

Bitters are usually strong alcoholic solutions, containing a small amount of vegetable material.

Vinegars are solutions, usually of organic substances, in dilute acetic acid, often aromatized. Alcohol and sugar will sometimes be present.

Decoctions are solutions of vegetable principles obtained by boiling the drug material with water.

Infusions are virtually the same as decoctions.

ELIXIRS, GLYCEROLES, ETC.

In the case of products falling under any of the above types, first note the odor and taste carefully, for the presence of many drugs and other substances can be detected at once by this means.

Next note the reaction of the product on litmus paper. Aromatic spirit of ammonia enters into the composition of some preparations, and acetic, phosphoric, hydriodic, and other acids are often present.

If there is sufficient sample it is well to distil a portion, test the vapors for ammonia or volatile acids, and examine the distillate for ethyl and methyl alcohol, and formaldehyde. Then evaporate the residual solution in the distilling flask on the steam-bath. Note the consistency of the residue; if much sucrose is present the crystals will be apparent and glycerin in any quantity will be observed at this point. Ignite a portion of this residue and note the quantity of ash. Test its reaction on litmus and on phenolphthalein. The presence of any quantity of inorganic material will be noted. Treat another portion of the residue with absolute alcohol; glycerin will dissolve and sucrose will be left behind.

Now proceed with a systematic examination of the sample in order to detect the various principles. Evaporate the alcohol if present. Separate a small portion of the residue and test for ammonium salts. If the product contains much sugar, continue the evaporation over the steam-bath until very concentrated. Treat residue with hot 95 per cent., or stronger, alcohol, stir thoroughly, cool, and decant alcohol. Repeat several times if necessary. This will separate the vegetable

principles from the sucrose, the gummy material, and most of the inorganic material, and the subsequent aqueous solution will be much easier to handle. Reserve the residue for future treatment (*A*). It should be noted that alcoholic solutions of milk-sugar dissolve some inorganic substances. Evaporate the alcoholic solution. The residue may contain alkaloids and their salts, glucosides and other vegetable principles, resins, synthetic organic substances, organic acids, glycerin, phenols, some sugars, tannins, coloring matters, some metallic salts of organic acids, and certain inorganic salts. Remove a small quantity of the residue on a glass rod, place on a watch-glass over a white surface, and add a few drops of ferric chloride solution; phenols, salicylic acid, and tannic acid will be indicated if present. Treat the balance with water, warm, and decant. Resin and certain gummy material will not go into solution. If anything remains undissolved, add a small quantity of normal sulphuric acid, but do not continue heating for any length of time. Decant acid solution into about two-thirds of the water solution, and if any precipitate forms at this point, stir and filter, wash precipitate thoroughly, and reserve filtrate and washings. Glycyrrhizin and certain substances in other drugs are precipitated on adding acid to an aqueous solution. If any material remained undissolved by the dilute acid, dissolve it in ether or chloroform, if possible, transfer to separatory funnel, shake out with normal acid, and filter acid solution into the main liquid. Evaporate the ether or chloroform, and examine residue for resin.

Place 1–2 c.c. of the acid solution in a test-tube and add a drop or two of Mayer's reagent; a precipitate

shows the presence of alkaloids. Treat another portion with Wagner's reagent (iodine in potassium iodide), and note whether a precipitate forms. If no precipitate occurs when Mayer's reagent is added, the possibility of the presence of alkaloids other than the xanthine bases is eliminated. If Wagner's reagent fails to give a precipitate, none of the alkaloids, nor a great number of other plant principles or many synthetics, are present. Now proceed with the separation by immiscible solvents. Shake out successively with petroleum ether, ether, chloroform. Evaporate each shake-out before proceeding with the subsequent solvent, and if anything is removed by a solvent, shake out at least three times with it. The residues should be examined according to the scheme of analysis already elaborated. Make solution slightly ammoniacal, and shake out with petroleum ether, ether, chloroform, and alcohol-chloroform, examining residues as above mentioned. The solution may still contain some organic substances which are not removed by immiscible solvents: certain glucosides and other principles, curarin, narcein.

Glycerin may be tested for in this solution. Evaporate with milk of lime until apparently dry. Extract with absolute alcohol, add three volumes of anhydrous ether, shake, and filter if necessary; evaporate solvents, and if the residue appears to be glycerin, identify it by borax-bead test, Mulliken's color reaction with sulphuric acid and pyrogallol, and Denigé's color tests,—page 68.

The balance of the solution, which was not treated with acid nor shaken out with immiscible solvents, should now be examined. Shake out from acid solution

with ether and then with chloroform; add ammonia, and shake out with some solvents. Now test the remaining aqueous solution for sugars, organic acids, and inorganic bases which might be present as salts of organic acids. The residue *A* above should now be examined. Remove a portion and test for sucrose, citrates, tartrates, acetates, albuminous material, hypophosphites, hypochlorites, peroxides, and other substances which may become altered by heat. Then ignite the balance of the residue at a low heat, but obtain an ash as free as possible from carbon. If very black, cool and treat with water, allowing the mixture to digest on the steam-bath. Then evaporate the water and ignite again. Caution is to be observed, as some of the alkali salts are volatile at a high temperature.

Treat the residue with water, filter if necessary, and perform the regular scheme of basic and acid analysis with the filtrate. Any material undissolved by water should be treated with acids, or, if still insoluble, fused with sodium carbonate and potassium carbonate, and the products examined for bases and acids. Examine a portion of the original material for arsenic by evaporating with a mixture of lime and magnesia water, igniting, and introducing the residue into the Marsh apparatus. Be sure the lime and magnesia are free from arsenic, or decompose with nitric and sulphuric acids.

Solutions containing large quantities of glycerin give up their active principles to immiscible solvents often with some difficulty, but by diluting considerably and shaking out with two or three portions of the solvent more than usually employed, the separation will be complete.

If a liquid preparation is designed for indigestion and stomach troubles, it should be tested for its action on starch and albumin, as described under "Digestives."

EMULSIONS

Emulsions are liquid preparations containing various substances, some in solution, and some held in suspension by gums, yolk of egg, etc. They are often employed as a means of presenting oily substances and aromatic balsams. A special classification has been reserved for oils and fatty materials, so after separating such substances from an emulsion, they should be examined according to the procedures given under that head.

Emulsions may contain acacia, tragacanth, Irish moss, Indian gum, dextrin, quillaja, or yolk of egg; sugar is sometimes present, saccharin, salicylic or benzoic acid, a few alkaloids, cod-liver and other oils, and hypophosphites, make up the list of the ordinary substances which are liable to be found. Alcohol is seldom met with.

Note the odor, taste, and reaction of the sample.

Before proceeding further, the emulsion should be broken. This may be done by diluting with water in a separatory funnel, and either agitating, heating, cooling with ice-water, adding a little alcohol, and, in rare instances, by lead acetate.

Add 1–2 c.c. normal sulphuric acid. Add ether and shake. This will dissolve the oily material. By using considerable of the solvent and adding a little alcohol, if necessary, a separation is not difficult. Draw off ethereal layer and repeat operation twice. Combine the ether solutions, and filter into another separatory

funnel. Shake out with a 5 or 10 per cent. solution of caustic alkali, which will remove any phenols, creosote, free fatty and other organic acids. Separate, evaporate the ether, and examine the residue for fixed oils and fats. Treat the alkaline solution with a slight excess of acid and shake out with ether. Separate and evaporate the ether, and examine the residue for phenols, creosote, salicylic or benzoic acid, and fatty acids. Next examine the aqueous layer containing the gums. Neutralize with ammonia, and evaporate ether to dryness over steam-bath, and treat the residue three times with alcohol, or concentrate to small bulk and add considerable alcohol, which will precipitate the gums. If the first procedure is used, evaporate the alcoholic solution obtained, treat the residue with water and a few c.c. of normal sulphuric acid, and then proceed with the treatment with immiscible solvents as described under liquid preparations of the previous class. The portion insoluble in alcohol should be examined for gums and metallic salts. If the second procedure is adopted, filter from the precipitated gum, evaporate the filtrate, treat the residue with water and normal sulphuric acid, and proceed with the treatment with immiscible solvents. Then evaporate and examine residue for metallic salts and salts of organic acids. Then examine the gummy residue on the filter.

LINIMENTS

These preparations, intended for external use, consist of solutions of camphor, menthol, cantharides, capsicum, turpentine, mustard oil, certain drugs as aconite, belladonna, opium, potassium iodide, iodine, and mercury, in

a menstruum of alcohol or chloroform; sometimes with ammonia and again in a menstruum of some fixed oil, croton, cotton-seed, sesame, almond, or an alcoholic solution of soap and occasionally glycerin or acetic acid, and often highly flavored with some aromatic oil as sassafras, peppermint, rosemary, or thyme. Products of this type should be examined carefully for methyl alcohol and acetone, as they are sometimes substituted for ethyl alcohol.

Examine first with litmus paper, first holding the moistened paper over the surface of the liquid which is being agitated. NH_3 and any volatile acid is readily detected in this way. Then test the liquid itself with litmus. If the mixture is acid, add a little sodium carbonate and then a small quantity of tannin. If alkaline, neutralize with tannin or with a mineral acid, subsequently treating with sodium carbonate and tannin. Dilute with water, place in a distillation apparatus, and distil until no more volatile oil and solvent come off. Then remove receiver and examine distillate. The volatile oils used can often be detected by their characteristic odors, with which one should have previously become familiar.

To obtain the alcohol in a state of comparative purity treat the distillate with sodium chloride until no more crystals will dissolve, then pour into a separatory funnel, add a few crystals NaCl in excess, and shake out two or three times with low-boiling petroleum ether. This removes the volatile oils and leaves the alcohol behind in the aqueous solution. After separating, distil the aqueous layer again and examine the distillate for both methyl and ethyl alcohols and acetone. This solution may still

contain camphor, but its presence will not affect the test for alcohol and acetone.

Evaporate the petroleum-ether layer at a low temperature and examine the residue for chloroform. In testing for non-volatile ingredients a fresh portion of the sample should be used. Evaporate over the steam-bath until no further decrease in the volume takes place. Watch the evaporation, and note whether any vapors of iodine are evolved; also hold a piece of paper moistened with starch solution in the vapors, and in the presence of iodine it will be turned dark blue. When no further diminution takes place, remove a small quantity of the residue, place it in a test-tube, add 1–2 c.c. of sodium hydroxide solution, and test for ammonium salts. Remove another small quantity and ash it. The presence of a comparatively large residue indicates that inorganic salts are present.

Now treat the residue with warm water and transfer to a separatory funnel, using ether if much oily material is present. Shake out with ether until all free oil and fats are dissolved; separate the ether layer and reserve for further examination. Should there be no oil or fat, this shaking out with ether may be dispensed with, but the idea of the procedure is to separate any free fats and oils from the fatty acids which will come from the soap if this is present. If any material remained in the evaporating dish, after treatment with water and ether, it should now be treated with dilute sulphuric acid, and the solution added to the liquid in the separatory funnel which has already been shaken out with ether. Note the appearance of any precipitate or turbidity in the aqueous liquid on the addition of the acid solution. Fatty acids from

soap will separate at this point. Shake out with ether, evaporate, and examine the residue for fatty acids, capsicum, mustard oil, phenol, cantharides (if these have not been removed in shaking out the fats). Now add ammonia in excess, and shake out successively with ether, chlorofrom, and chloroform-alcohol 2 : 1. Examine residues for alkaloids, particularly aconite (with care, remembering that the solution under examination is for external use), belladonna, and opium alkaloids. Evaporate off any solvent and excess of ammonia, and examine the solution for glycerin and inorganic salts. If desirable, evaporate a fresh portion of the sample, ignite at a low temperature, and examine the ash. The ethereal solution containing the free fats and oils should now be examined in detail. Shake out first with dilute sodium hydroxide, and test this solution for phenols. Then evaporate ether and examine residue for capsicum and cantharides, and identify the fixed oil or fat. The above procedure is general for a liniment containing any or all of the ingredients which might occur. In many cases it can be greatly simplified, as one will determine as the analysis proceeds.

TOOTH WASHES AND GARGLES

These are usually antiseptic solutions, either acid or alkaline in reaction, the acidity being due to boric acid, and the alkalinity to sodium or potassium salts.

In general a gargle is an aqueous or hydroalcoholic solution of boric acid, borax, sodium bicarbonate, sodium benzoate, sodium phosphate, sodium sulphate, potassium chlorate, potassium carbonate, ammonium chloride,

containing the oils of gaultheria, eucalyptus or eucalyptol, pinus pumilio, coriander, and often with formaldehyde, hydrogen peroxide, carbolic acid, and thymol.

In the tooth washes the composition will run to soap and glycerin with the above-mentioned flavors, together with the oils of cassia and clove and tincture of myrrh. They will often be colored with cudbear, cochineal, rosolic acid, methyl orange, and salts of berberine. If alcohol is found it should be examined carefully to determine whether it consists wholly or in part of methyl alcohol. First test the solution with litmus paper; note the odor and taste, distinguishing, if possible, any of the aromatic constituents and oils used in flavoring. Make special tests for formaldehyde, hydrogen peroxide. Place the solution in a distillation flask, dilute with water, and distil until alcohol is all over. Examine the distillate for alcohol, and make special test for methyl alcohol. If essential oils are present in quantity, they should be removed as described under "Liniments." If formaldehyde is present in the sample, it will come over with the distillate, and must be removed before testing for alcohol. This may be accomplished by adding an excess of metaphenylenediamine hydrochloride, which forms an insoluble precipitate with the formaldehyde. Re-distil and examine the distillate for alcohols. Residue in distillation flask divide into two parts. Place one portion in separatory funnel and add dilute sulphuric acid; extract with ether and examine ether residue for benzoic acid, phenol, or other substances which might be removed. If the preparation under examination contains a soap the fatty acids will appear at this point. Then shake out with chloroform and

examine residue. Add ammonia in excess and extract successively with ether and chloroform, examining any residue for alkaloids. Then evaporate the residual solution and examine residue for glycerin. Ignite at a low temperature, and examine ash for inorganic salts. The second portion should be examined for ammonium salts, sulphates, free boric acid, and also the dye present.

SOLID EXTRACTS, POWDERED EXTRACTS, AND CONCENTRATIONS

These products alone are among the least common of any substances that claim the attention of the drug analyst. They often take part in the preparation of pharmaceuticals, but alone, one is seldom called to analyze them, and when they are sold in this way they are usually labelled so that an identification is not difficult.

They are virtually evaporated fluidextracts of the plants, and can be examined in practically the same way as the liquid. In case it is desired to identify the particular plant principle, the substance should be dissolved in alcohol, and evaporated with water or weak acid (acetic in case the active principle is unstable or suspected to be so), until the alcohol has been driven off, and then the liquid cooled, filtered, and the filtrate shaken out in turn with the various solvents, and examined as described under the schemes for testing for alkaloids, glucosides, and miscellaneous active principles.

Having identified the constituents, a quantitative determination follows according to the nature of the substance found. The Pharmacopœia has set a standard for a number of solid extracts, and assay methods are

given under them. In other cases a procedure similar to that adopted for the fluidextract in question may be applied.

Concentrations are usually the principles of various plants, in a more or less purified state. Some of the more common are:

Aletrin (Star-grass; Unicorn Root)
Apocynin (Bitter Root)
Asclepidin (Pleurisy Root)
Baptisin (Wild Indigo)
Cascarin (Cascara Sagrada)
Caulophyllin (Blue Cohosh)
Cimificugin (Black Cohosh)
Cornin (Dogwood)
Cypripedin (Ladies' Slipper)
Digitalin (Foxglove)
Dioscorein (Wild Yam)
Euonymin (Wahoo)
Gelsemperin (Gelsemium)
Hamamelin (Witch Hazel)
Helonin (Helonias; False Unicorn)
Irisin (Blue Flag)
Juglandin (Butternut)
Leptandrin (Culver's Root)
Lupulin (Humulus Lupulus; Hops)
Phytolaccin (Poke Root)
Podophyllin (Mandrake)
Sanguinarin (Blood-root)
Scutellarin (Scullcap)
Senecin (Life-root)
Viburnin (Cramp-bark)

PILLS, TABLETS, LOZENGES, TROCHES, PASTILS

In the composition of pills and tablets one is liable to find about everything in the realm of pharmaceutical chemistry; new formulas are springing into existence every day, and the number of combinations is legion.

Pills usually have some form of mass as a basis, and in this the medicament is incorporated. The base may contain glucose, honey, soap, syrup, glycerin, tragacanth, vaselin, lycopodium, starch, confections, acacia, mastic, gypsum, kaolin, dextrin, and charcoal. The product after mixing is usually coated, and this coating may consist of sugar, with or without color, gelatin, gold, silver, keratin (in the case of enteric pills intended to go through the stomach unchanged, and dissolve in the intestines).

There are also pills made by a powder process without a mass base, and sometimes called "friable pills."

Tablets include triturates and compressed tablets with or without sugar or chocolate coating, this last often being a salt of iron instead of "chocolate." Triturates are made up with milk sugar as a base. Excipients are often used with compressed tablets, but the material is usually of such a nature that it can be mixed in the dry state, and the shape of the product is obtained by compression.

Lozenges and troches do not have as wide an application as do pills and tablets, hence the number of possible formulas is much smaller. They consist of powders incorporated with sugar and mucilage, sometimes licorice, currant paste, and the like.

Pastils are usually made up with a base consisting en-

tirely of gum, such as acacia. Their use and consequent variety is limited.

In the case of all preparations coming under this class, with the exception of the pastils, first crush the sample in a mortar, noting particularly the odor which will suggest the presence of many substances. Taste some of the powdered sample. Pastils do not crush readily, and should be treated differently. Moisten a small quantity with water, and note its reaction on litmus paper. Also test with phenolphthalein both before and after warming; bicarbonate will be indicated by giving no color with phenolphthalein until heat is applied. Ash a portion of the powder, and, if there is much residue, inorganic salts are indicated. Test the reaction of the ash with phenolphthalein. Preparations which are neutral or acid before ignition, and alkaline afterward, contain alkali salts, or plant material. Examine the powder under the microscope; many plant substances can be identified in this way. It may be necessary to get rid of some of the other material by washing with water or floating in a solution of zinc sulphate or Mayer's reagent. Treat some of the powder in a dry test-tube with a few drops of concentrated sulphuric acid. Note any effervescence in the cold, also the odor given off, and test the gases with lime-water, lead acetate paper, starch-paper, etc. If no action occurs in the cold, warm gently, and note the result. Charring will generally occur on heating, owing to the prevalence of sugar. Test powder for ammonium salts. Test powder for arsenic.

Triturate the ground material from 6–12 or more of the pills or tablets with 95 per cent. or stronger alcohol. Filter the menstruum and repeat twice. Preserve any

undissolved material for future treatment. Evaporate the alcoholic solution. Note the quantity and appearance of the residue. Test a small portion with ferric chloride, and note the color; tannins, salicylates, phenol derivatives, may be indicated here. Treat the balance with water and warm gently; decant if not completely soluble, treat the residue with normal sulphuric acid, and again warm. If the substance is still unacted upon, treat with ether or chloroform, place in a separatory funnel, and shake out with normal sulphuric acid, adding acid extract to about two-thirds of the other aqueous liquid. Note any precipitate formed on the addition of sulphuric acid; licorice is often present, and the glycyrrhizic acid will precipitate at this point. Remove a small portion of the solution and test with Mayer's and Wagner's reagents; alkaloids are indicated if the former produces a precipitate. If no precipitate is obtained with either of the above reagents, the possibility of the presence of a large number of organic substances is eliminated. Proceed now with the shaking-out process with immiscible solvents, evaporating and examining each extract in turn before proceeding with the subsequent solvent. When the final shaking out is completed, evaporate the solution to drive off the excess of solvents and ammonia. The residual solution should be examined for organic acids, certain substances which are known to be left behind by immiscible solvents, as glycerin, sugars, and metals which might be present as salts of organic acids.

The portion of the ground sample insoluble in alcohol should be examined for sugars, starch, albumin, organic salts, and gums. Treat with water, and proceed with

the aqueous solution according to the scheme of basic inorganic analysis.

The above procedure is recommended as it gives one an insight into the actual composition of the product better than by ignition and subsequent examination of an aqueous or acid solution of the residue. On igniting certain substances their composition is changed to such an extent that the form in which they originally existed is lost. However, it is well to make an ignition of the preparation, and run through an analysis of the ash both as confirmatory, and possibly for detecting substances which may have been overlooked. In many instances it may be necessary to adopt special schemes for the particular preparation under examination, and experience will demonstrate when such a measure is necessary.

If the product is claimed to have digestive properties determine its action on egg albumin and on starch solution; details of which procedure are elaborated under "Digestives."

PASTILS

Dissolve the sample in as small a quantity of water as possible. Note odor and reaction to test-papers and solutions. Test a portion for ammonium salts. Add a small amount of normal sulphuric acid, then pour the solution into a considerable excess of alcohol, from 5 to 10 times the amount of the aqueous solution, allow the mixture to stand until the precipitated gums have settled out and then filter. Evaporate the alcoholic solution after neutralizing with ammonia. Examine the residue the same as powdered pill or tablet.

The portion precipitated by alcohol should be

examined as described under the portion of the powdered pill or tablet which was insoluble in alcohol.

POWDERS, CACHETS, HARD CAPSULES, AND DUSTING POWDERS

Powders in general may be composed of a great variety of substances, but an individual powder is generally of simple composition.

A cachet is a powder offered in a protective coating, *e.g.*, conseals.

Hard capsules contain a variety of substances, but the contents are easily removed and may be examined the same as other powders. Hard capsules will often contain solid extracts, which can be removed and then examined as described under solid extracts.

Dusting powders will contain only a limited variety of material. They may contain talc, boric acid, salicylic acid, zinc oxide, chloretone, lycopodium, and starch, flavored with violet, rose, orris, etc.

Tooth powders will contain chalk and powdered soap.

In general these products may be examined by the same procedure recommended for pills and tablets.

GLOBULES AND SOFT CAPSULES

These products usually consist of a liquid, sometimes with a solid in suspension, enclosed in an air-tight gelatin covering.

Soft capsules are made with flexible gelatin, and are of different sizes. Gobules are usually of one size and the gelatin is firmer.

Some of the more important therapeutic agents administered in the form of capsules and globules are castor oil, cod-liver oil, copaiba, creosote, santalwood oil, cassia oil, turpentine, chaulmoogra oil, methyl salicylate, apiol, methylene blue, salol, oleoresin of cubeb, etc.

The individual formulas are not very complex, and nearly all of the ingredients are indicated at once by some physical characteristic. Copaiba, santalwood oil, cassia oil, methyl salicylate, and cresote are readily detected by their odor, and the deep blue color of methylene blue is unmistakable.

The contents should be removed and examined according to the schemes described under the respective headings for a liquid, a solid, or an oily material.

Pills or tablets in suspension can be separated from the oils by treating the mixture with ether.

In case the analyst experiences difficulty when working with a product containing a large quantity of a volatile oil, the latter may be separated by steam distillation.

EFFERVESCENT PREPARATIONS AND ARTIFICIAL MINERAL-WATER SALTS

Effervescent preparations nearly always contain sodium bicarbonate, tartaric acid, sugar, and the medicinal ingredients. In case the product is in granular form citric acid will also be present.

The medicinal ingredients are limited, and are in such a form as to be readily soluble in water. Remedies for headache are often exhibited in this form, and lithium

compounds, magnesium salts, and salicylates are commonly found.

Artificial mineral-water salts consist of inorganic salt mixtures, in which the sulphates, chlorides, bicarbonates, and carbonates of the alkalies and magnesium predominate. Formulas of the composition of some of the most prominent on the market are given in Merck's Index, page 385.

An aqueous solution of an effervescent preparation should be acidulated with normal sulphuric acid, and some of the solution tested with Mayer's and Wagner's reagents to detect alkaloids and other organic substances. Then shake out with immiscible solvents from both acid and ammoniacal solution, examining each residue according to the regular scheme. The residual solution should now be evaporated, and after the excess of solvents and ammonia are removed, the residue should be examined for organic acids and metallic salts. Examine for pepsin and other digestives.

An artificial mineral-water salt should be examined by following the regular schemes for basic and acid inorganic analysis.

PASTES, OINTMENTS, AND EMOLLIENTS

Pastes and creams may or may not contain an oil or fatty material, and if ingredients of that nature are present, the product is virtually an ointment, and the method of procedure would be the same as for the latter. The semi-fluid nature of pastes may be due to glycerin or to some nitrogenous substance, such as moist casein. Tooth pastes contain a considerable quantity of cal-

cium carbonate, and sometimes calcium phosphate, soap, occasionally pumice, essential oils, and coloring matter.

Creams made up with a casein base will usually be found to contain zinc oxide, coloring matter, essential oils, and salicylic acid or similar preservative.

Emollients are made up sometimes with a base of glycerin, and again with mucilage of Irish moss or the like, and will contain no fixed oil or fat. Starch and boric acid are usually present.

Ointments consist of a base of petrolatum or some fixed oil or fat, often with inorganic substances in suspension, sometimes alkaloidal bodies dissolved as oleates in suspension, camphor, aromatic substances, synthetics, and various other organic bodies. Coloring and flavoring agents are often present. The composition may be as variable as the liquid products. The presence of an oil or a fat is usually apparent from a very cursory examination of the sample. If there is any doubt, treat a small portion with water and warm, when any fixed oil or fat will melt and separate out on the surface. Note the odor. If neither oil nor fat is present, treat with warm water until nothing further dissolves. If starch or gums are present, it may be necessary to break up the emulsion with alcohol, then filter again, and evaporate off the alcohol. Reserve the residue for future examination and proceed as follows with the solution:

Note the reaction to litmus; to a portion add dilute sulphuric acid and note any precipitate; if soap is present the fatty acids will separate at this point. Shake out with immiscible solvents, and examine the residues for fatty acids and other organic substances,

though very few of the latter are liable to be met with. The solution should now be evaporated until free from solvents and ammonia, and examined for inorganic material and organic substances, glycerin, gums, etc., not removed by immiscible solvents; or the portion of the solution which was not acidified in the first place may be used. The material insoluble in water should now be examined for those organic substances which do not dissolve in water, and also for inorganic material. It is well to dry it first, and then treat with alcohol, which will dissolve out most of the organic substances except starch and gums.

Ointments and pastes with oils or fatty bases must be examined somewhat differently: Note the odor; transfer to an Erlenmeyer flask and cover with ether. Shake until all the fatty material, oils, waxes, and the like have gone into solution. Filter the ether solution through a creased filter. Repeat if necessary until all the fatty material has dissolved, using a glass rod to break up resistant waxes. Wash the residue on the filter paper with ether until it is free from grease, and set it aside for future examination. Transfer the ethereal solution to a separatory funnel and shake out with dilute sulphuric acid. The acid will remove organic substances of a basic nature, *e.g.*, alkaloids, if they had been present in the free state or as oleates. To a small portion of the acid solution freed from any adhering ether by warming, add Mayer's reagent and also Wagner's reagent, and note any precipitate. If alkaloids or other organic substances are indicated, render the balance of the solution alkaline with ammonia, shake out with immiscible solvents, and examine residue so as to identify the substances present.

Then shake out the ethereal solution with 10-per-cent. sodium hydroxide. The alkali will remove the free fatty acids, other organic acids, certain dyes, acid resins, phenols, etc. Separate the alkaline solution, acidify, and shake out with ether. Filter and evaporate the ether solution which will leave the dissolved substances in such a form that they can be separated and identified. The ether solution may now contain hydrocarbons, paraffin, cerasin, petrolatum; fixed oils, fats and waxes, turpentine, camphor, menthol, some of the higher alcohols, neutral resins, etc. Evaporate carefully to prevent loss of volatile constituents. Examine the residue to identify any fixed oil or fat. Alcohol will separate the turpentine, camphor, menthol, etc., and saponification of the residue and examination of the fatty acids separated by acid and shaken out with ether will aid in identifying the oils, while the unsaponifiable residue will contain the inert hydrocarbons.

The residue on the filter which was insoluble in ether should now be examined. Treat with hot water, filtering if any material remains undissolved. Divide the solution into two portions, reserving one for any special tests that may be necessary. Treat the other portion with immiscible solvents in order to detect alkaloids, glucosides, synthetics, and other organic substances possibly present. Then examine the residue for metallic salts. If any residue was left from the treatment with water, it should be dissolved in acid if possible and the solution examined for metallic salts insoluble in water. If any material remains undissolved by acids, examine it for substances known to be left by that treatment.

INHALANTS

These preparations are usually made up with an oily base, though specimens will be found in which no oil is present, the lubricating medium being glycerin. Those of the latter type may be examined according to the general scheme given under liquids.

The oily type have as a base liquid petrolatum, and sometimes other oils such as sweet almond, olive, and the like; copaiba, oil of tar, oil of eucalyptus and eucalyptol, carbolic acid, Tolu, Peru, guaiacol, creosote, tincture of iodine, iodoform, camphor, thymol, cocain, adrenalin, chloretone, acetozone, ether, and alcohol may all be suspected.

The procedure of analysis should be the same as under ointments.

SUPPOSITORIES, CRAYONS, BOUGIES

Suppositories are made up on either a base of cacao butter (oil of theobroma), or glycerin mixed with sodium stearate; soap is used and wax and spermaceti are sometimes mixed to stiffen the base.

The medicinal ingredients vary according to the use. Rectal suppositories used for pile remedies often contain opium, tannic acid, and lead acetate. Iodoform, morphin, belladonna, carbolic acid, and other antiseptics will be found, the latter especially in vaginal suppositories and bougies which are used in gonorrheal affections. Vaginal suppositories will also consist of boric acid, thymol di-iodide, acetanilide, glycerin, ichthyol, iodine,

golden seal alkaloids (hydrastin, etc.), chloretone, certain salts of zinc, salts of metals with organic acids as nucleinic, and the like.

Bougies which are used in the urethra will contain gelatin and some gums, but in other respects they are essentially of the same general composition as the other suppositories.

An examination should follow the general lines given under pastes and ointments.

PLASTERS

These products are intended to be adhesive at the temperature of the human body. The base may consist of rubber, Burgundy pitch, gum olibanum, galbanum, rosin, Canada balsam and other resins and gums, wax, soap, lead oleate, etc. A preliminary examination will usually give one an idea as to which is present.

The medicament may consist of aconite, belladonna, opium, arnica, capsicum, ginger, phytolacca, cantharides, camphor, asafetida, gum ammoniac, mercury, iron, lead oleate, etc.

Place the sample in a beaker and cover with ether. If it does not dissolve readily in this solvent, replace with chloroform, and soak until nothing further will go into solution. Filter into a separator. The insoluble material may consist of soap, inorganic and organic salts, diluent, inert plant constituents, and the cloth on which the plaster was spread.

Dry the insoluble residue and treat with water. Filter, and if anything remains undissolved examine it for starch, metals, and metallic salts insoluble in water.

Transfer the aqueous solution to a separator, and add normal sulphuric acid, noting any separation of fatty acids due to soap. Extract with immiscible solvents, then make alkaline with ammonia, continuing the extraction with immiscible solvents, and examine carefully the residue left on evaporation. Finally test for the presence of metallic salts soluble in water.

The ether or chloroform solution originally obtained should now be investigated. Add dilute sulphuric acid to the separatory funnel and shake thoroughly. Lead will become apparent at this point, due to the separation of lead sulphate. Draw off the aqueous layer, and continue the addition and extraction with acid until no more separation of lead results. Reserve the ethereal or chloroformic solution. Filter the combined acid extracts, and examine the insoluble substances for lead. To a small portion of the filtered liquid, previously warmed to expel any adhering solvent and then cooled, add a drop of Mayer's reagent, and the presence of an alkaloid will be indicated by the characteristic precipitate. If no precipitate occurs, add Wagner's reagent. If no precipitate is obtained with either of these reagents, there is little need of testing further for alkaloids. If, however, the latter are indicated, add ammonia to the balance of the solution and shake out with immiscible solvents, examining the residues to determine the particular substance present.

Next shake out the solvent solution with 10-per-cent. sodium hydroxide, two or three times. Combine the alkaline extractions, acidify with sulphuric acid, shake out with immiscible solvents, and examine residues. Oleic acid from lead oleate will appear at this point; also resin acids,

phenols and other substances having acid properties.

Then evaporate the ethereal solution and examine the residue for neutral principles.

DIGESTIVES

Preparations intended to relieve stomach troubles and indigestion should be specially examined in order to determine their action on starch and egg albumen, though the rest of the analysis may follow the general procedure outlined for the particular class of products under investigation.

In order to test its action on egg albumen, about 5 to 10 grams of the sample, if it is a solid, are ground in a mortar, 10 c.c. dilute hydrochloric acid (9 c.c. dilute $HCl + 291$ c.c. H_2O) added, well incorporated with the powder with the pestle, and filtered, this procedure being repeated until the filtrate measures 50 c.c. If the sample is a liquid it can be added directly to the egg albumen. The balance of the test should follow the directions given in the Pharmacopœia for the determination of pepsin, and a blank test performed at the same time for comparison.

To determine whether or not the sample has any action on starch, it is first necessary to demonstrate the presence or absence of substances reducing Fehling's solution; if absent, the procedure is much simplified, as one needs but prove that the preparation has the power to change starch into reducing sugar. If reducing substances occur naturally, a quantitative determination must be carried out, in one case with a known amount of the sample, and in another after the same quantity has

been applied to a starch solution. To perform the starch test about 20 grams of neutral potato starch are suspended in 30 c.c. cold water, and after being well mixed the mixture is poured into about 900 c.c. of boiling distilled water, the whole well stirred and boiled for about ten minutes until a homogeneous jelly is obtained, and then cooled rapidly to 40° C. Now provide a number of cylindrical glass tubes which will hold about 100 grams of starch paste, nearly immerse these in a water-bath heated to 40°, and allow to stand until the contents have attained this temperature. The digestive solution may then be added, and the tube closed with a rubber stopper and shaken vigorously. It is then returned to the water-bath and digested for ten minutes, the tube being shaken from time to time.

The product which is to be examined for its action on starch should be treated with water, and all acid or alkali avoided. If it is in the liquid form, it may be added directly to the starch paste.

SCHEME FOR THE RAPID DETECTION OF INHIBITED DRUGS

If the product is a liquid, on distillation chloroform and a trace of acetanilide will be obtained.

Chloroform will be recognized by its settling out as a heavy liquid at the bottom of the flask unless there is a large excess of alcohol. The water should be decanted, and an isonitrile test performed: A small quantity of strong KOH solution is added, the mixture warmed and a drop of anilin added, when in the presence of chloroform the disagreeable odor of phenyl isocyanide will be noted. In case a trace of acetanilide distilled over with the chloroform originally, the disagreeable odor will be apparent at once on warming with KOH. However, as a matter of fact, chloroform and acetanilide will seldom, if ever, be found in the same preparations.

Further tests for recognizing chloroform, Allen, Vol. 1, p. 274.

Chloroform occurs in liniments, cough mixtures, and anesthetics.

The solution, after distillation, or, if the original product was a solid, a solution made from it, is rendered slightly acid with dilute sulphuric acid, and then placed in a separatory funnel and shaken with ether three times. The ether solutions are separated and evaporated and the residue may contain:

Acetanilide, mpt. 110–113°
Acetphenetidin, mpt. . . . . 135°
Hydrated chloral. liquid

Place a watch glass over the beaker or dish in which the

evaporation was made and place over the steam-bath, noting any sublimate. Acetanilide readily sublimes, and the sublimate may be tested for the isonitrile reaction with chloroform and KOH.

A portion of the residue is warmed with dilute sulphuric acid over the steam-bath, continuing the evaporation until the volume has diminished about one-half. Cool the liquid, and add a few drops of potassium bromide-bromate reagent. In the presence of acetanilide a yellowish-white precipitate will appear, and in the presence of acetphenetidin a blue color. This test will detect both when they occur together. (The bromide-bromate reagent is made by adding bromide in slight excess to a concentrated aqueous solution of KOH, diluting to dissolve any separated salts, and boiling to expel any excess of bromine.)

To test for hydrated chloral treat the residue with a small amount of water, add a few drops of ammoniacal silver nitrate and warm, when a reduction indicates chloral. Warm a second portion of the aqueous solution with Fehling's solution, which will be reduced by chloral.

Hydrated chloral will also give the isonitrile reaction when tested by the same procedure as was done in the case of chloroform.

In case both chloral and acetanilide were present in the same mixture, one would obtain the isonitrile reaction at once on adding alkali.

For further tests see the following references:

Acetanilide, Allen, Vol. 6, p. 83, U. S. P.

Acetphenetidin, Allen, Vol. 6, p. 99, U. S. P.

Hydrated chloral, Allen, Vol. 1, p. 269.

Now shake out the solution three times with chloro-

form in order to remove any of the above substances remaining behind in the solution, and others which will be removed in the presence of acid.

Add dilute KOH until the solution is alkaline to litmus, and then shake out three times with petroleum ether. The following substances will be removed:

Cocain—crystals mpt. 98°;

Beta-Eucain—oil;

Alpha-Eucain—mpt. 104°–105° (very seldom found).

Remove a portion of the residue on the end of the finger and rub it gently over the tip of the tongue; in the presence of any of the above substances a numbness will soon develop, persisting for some time in case the amount is large.

Dissolve the residue in petroleum ether, and pour a small quantity into an evaporating dish. Evaporate the solvent, treat residue with 1 c.c. concentrated nitric acid, and evaporate to dryness over the steam-bath; while residue is still warm add a few drops of $N/_1$ alcoholic KOH and note whether there is any odor of ethyl-benzoate. Cocain will give this pleasant-smelling substance, while neither of the eucains will. Run a comparative test until familiar with the odor.

Evaporate a small portion of the ethereal solution on a microscope slide, treat with very dilute sulphuric acid, and add a drop of gold chloride solution, noting the appearance of the crystals formed under the microscope.

Perform this latter test using platinum chloride solution and palladium chloride solution; both reagents give characteristic crystals with the above alkaloids.

References:

Cocain, Allen, Vol. 6, p. 321, U. S. P.

Beta-Eucain, Hager, Vol. 1, p. 1059.

Alpha-Eucain, Hager, Vol. 1, p. 1059.

Now shake out with sulphuric ether, which will remove the following substances:

Codein (methyl morphin) mpt. 152°–159°;

Dionin (ethyl morphin) mpt. of free base 89°–90°;

Heroin (diacetyl morphin) mpt. of free base 171°;

Apomorphin;

Peronin (Benzylmorphin).

Separate the residue obtained into a number of fractions in small porcelain evaporating dishes, and perform tests with color-producing reagents as indicated on chart accompanying page 79.

Codein differs from dionin by the fact that the free base is more readily soluble in ammonia.

Heroin on treatment with alcohol and sulphuric acid gives the odor of ethyl acetate.

Codein and heroin are the only two products in this fraction which will be met with to any extent.

References for further tests:

Codein, Allen, Vol. 6, p. 390, U. S. P.

Dionin, Hager, Vol. 2, p. 404, and appendix, p. 494.

Heroin, Allen, Vol. 6, p. 389.

Apomorphin, Allen, Vol. 6, p. 387, U. S. P.

Peronin, Hager, Vol. 2, p. 404.

Now shake out the solution three times with chloroform and discard the chloroform. Then shake out the alkaline liquid three times with a mixture of chloroform and alcohol 2 to 1. Separate and evaporate the solvent and the residue may contain:

Morphin, mpt. 254° on rapid heating.

Test according to the scheme on the color chart.

For references see Allen, Vol. 6, p. 374, U. S. P.

REAGENTS—SOLUTIONS

The solutions recommended for use in connection with this work have been made to conform as nearly as practicable with those given in the Pharmacopœia, and directions for preparations are given on the basis of 100 c.c. quantities.

Acid Acetic Glacial

" Acetic 36%—35 c.c. glacial acid with 65 c.c. water.

" Acetic Dilute 10%—6 c.c. glacial with 94 c.c. water.

" Hydrochloric Conc.

" Hydrochloric Dilute 10%—30 c.c. hydrochloric acid conc. with 70 c.c. water.

" Nitric Conc.

" Nitric Dilute 10%—11 c.c. nitric acid conc. with 89 c.c. water.

" Sulphuric Conc.

" Sulphuric Dilute 10%—7 c.c. sulphuric acid conc. with 93 c.c. water.

Alcohol 95%.

Ammonia Water (Stronger) 28%.

Ammonia Water Dilute 10%—36 c.c. stronger ammonia water with 64 c.c. water.

Ammonium Carbonate. 20 grams ammonium carbonate U. S. P. dissolved in 20 c.c. ammonia water 10% and 80 c.c. water.

Ammonium Molybdate. 10 grams molybdic acid dis-

	solved in 42 c.c. ammonia water 10% and poured into a mixture of 63 c.c. water and 63 c.c. nitric acid conc.
Ammonium Oxalate.	4 grams dissolved in 100 c.c. water.
Ammonium Sulphate.	10 grams dissolved in 100 c.c. water.
Ammonium Sulphide.	60 c.c. ammonia water 10% are saturated with hydrogen sulphide and then diluted with 40 c.c. ammonia water 10%. To prepare the yellow ammonium sulphide add 1–2 grams of sulphur and shake until dissolved.
Ammonium Vanadate (Mandelin's Reagent).	1 gram dissolved in 100 c.c. sulphuric acid conc.
Barium Chloride.	10 grams dissolved in 100 c.c. water.
Barium Hydroxide.	Saturated solution.
Bromine Water.	1 c.c. dissolved in 100 c.c. water. Freshly prepared.
Calcium Chloride.	10 grams dissolved in 100 c.c. water.
Calcium Hydroxide.	Saturated solution.
Calcium Hypochlorite.	10 grams triturated with 20 c.c. water, filtered and repeated and the filtrate made up to 100 c.c.

Calcium Sulphate.	Saturated solution.
Chlorine Water.	0.5 gram potassium chlorate treated with 2 c.c. hydrochloric acid conc. in a flask fitted with a perforated stopper, warmed on steam-bath and when the flask is full of gas add 100 c.c. water.
Cobalt Nitrate.	10 grams dissolved in 100 c.c. water.
Copper Sulphate.	10 grams dissolved in 100 c.c. water.
Fehling's Solution.	1. 7 grams copper sulphate dissolved in 100 c.c. water. 2. 35 grams Rochelle salt and 10 grams sodium hydroxide dissolved in 100 c.c. water.
Formaldehyde-Sulphuric Acid.	10 c.c. formaldehyde solution in 50 c.c. sulphuric acid conc.
Iron Chloride (Ferric).	10 grams dissolved in 100 c.c. of recently boiled water.
Gold Chloride.	3 grams dissolved in 100 c.c. water.
Iodine (Wagner's Reagent).	2 grams with 6 grams potassium iodide dissolved in 100 c.c. water.
Lead Acetate.	10 grams dissolved in 100 c.c. water.

Lead Subacetate.	18 grams lead acetate dissolved in 70 c.c. water, added to 11 grams of lead oxide (litharge PbO) in a porcelain dish, boiled for ½ hr., filtered and made up to 100 c.c.
Magnesia Mixture.	10 grams magnesium sulphate and 20 grams ammonium chloride dissolved in 80 c.c. water and 42 c.c. ammonia water 10% added.
Mercuric Chloride.	5 grams dissolved in 100 c.c. water.
Mercuric Chloride, Alcoholic.	6 grams dissolved in 100 c.c. alcohol 95%.
Mercuric-Potassium Iodide (Mayer's Reagent).	1.3 grams mercuric chloride dissolved in 60 c.c. water added to 5 grams potassium iodide dissolved in 10 c.c. water and made up to 100 c.c.
Palladous Chloride.	5 grams dissolved in 100 c.c. water.
Phenolphthalein.	1 gram dissolved in 50 c.c. alcohol and 50 c.c. water added.
Phosphomolybdic Acid (Sonnenschein's Reagent).	Prepare ammonium phosphomolybdate and, after washing with water, boil with nitric acid to expel

	ammonia, evaporate to dryness and dissolve in 10% nitric acid.
Phosphotungstic Acid (Scheibler's Reagent).	20 grams sodium tungstate and 15 grams sodium phosphate dissolved in 100 c.c. water containing a little nitric acid.
Picric Acid (Hager's Reagent).	1 gram dissolved in 100 c.c. water.
Platinic Chloride.	13 grams dissolved in 100 c.c. water.
Potassium-bismuthic Iodide (Dragendorff's Reagent).	8 grams bismuth subnitrate dissolved in 20 c.c. nitric acid and mixed with 28 grams potassium iodide dissolved in a little water, filtered and made up to 100 c.c.
Potassium Bromide-Bromate.	To a concentrated solution of potassium hydroxide add bromine to saturation, boil off excess, and dilute with an equal volume of water.
Potassium-cadmium Iodide (Marmé's Reagent).	2 grams cadmium iodide added to a boiling solution of 4 grams potassium iodide in 12 c.c. water and mixed with an equal volume of saturated solution potassium iodide.

Potassium Bichromate.	10 grams dissolved in 100 c.c. water.
Potassium Chromate.	10 grams dissolved in 100 c.c. water.
Potassium Ferricyanide.	10 grams dissolved in 100 c.c. water freshly made.
Potassium Ferrocyanide.	10 grams dissolved in 100 c.c. water.
Potassium Hydroxide.	6 grams dissolved in 94 c.c. water.
Potassium Iodide.	20 grams dissolved in 100 c.c. water.
Potassium Permanganate.	0.5 gram dissolved in 100 c.c. water.
Potassium Sulphocyanide.	1 gram dissolved in 100 c.c. water.
Silver Nitrate.	5 grams dissolved in 100 c.c. water.
Silver Nitrate, Ammoniacal.	5 grams silver nitrate dissolved in 100 c.c. water and treated with ammonia water 10% until precipitate is not quite redissolved.
Sodium Bitartrate.	3.5 grams tartric acid boiled with 80 c.c. water, sodium carbonate added until neutral and then 3.5 grams tartric acid added and solution made up to 100 c.c.
Sodium Carbonate.	10 grams dissolved in 100 c.c. water.

Sodium-Cobaltic Nitrite.	4 grams cobalt nitrate and 10 grams sodium nitrite dissolved in 50 c.c. water, 2 c.c. acetic acid 36% added and then water to 100 c.c.
Sodium Hydroxide.	6 grams dissolved in 94 c.c. water.
Sodium Hypochlorite.	9 grams calcium hypochlorite triturated with 20 c.c. water, filtered and repeated, and washed with 10 c.c. water, filtrate mixed with 6.5 sodium carbonate monohydrated dissolved in 30 c.c. water, filtered, washed and made up to 100 c.c.
Sodium Nitroprusside.	1 gram dissolved in 19 c.c. water. Freshly prepared.
Sodium Phosphate.	10 grams dissolved in 100 c.c. water.
Stannous Chloride.	Pure tin boiled with hydrochloric acid conc. having metal in excess; when saturated, crystals will form, which are separated and drained and dissolved in 10 parts water and the solution preserved in a well stoppered bottle containing tin foil.

Starch.	0.5 gram starch mixed with 10 c.c. water and added to 90 c.c. boiling water.
Sulphomolybdic Acid (Froehde's Reagent).	10 grams molybdic acid or sodium molybdate dissolved in 100 c.c. sulphuric acid conc.
Tannic Acid.	10 grams dissolved in 10 c.c. alcohol and 90 c.c. water added.

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